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H. Scott Fogler Third Edition

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H. Scott Fogler

Elements of Chemical Reaction Engineering

Third Edition

Prentice Hall International Series
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Third Edition

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of Chemical Engineering
The University of Michigan, Ann Arbor



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Dedicated to the memory of

Professors

Giuseppe Parravano
Joseph J. Martin
Donald L. Katz

of the University of Michigan
whose standards and lifelong achievements
serve to inspire us

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Preface

"The man who has ceased to learn ought not to be allowed to wander around loose in these dangerous days."

*M. M. Coady
(ca. 1870)*

A. The Audience

This book is intended for use as both an undergraduate- and graduate-level text in chemical reaction engineering. The level of difficulty will depend on the choice of chapters to be covered and the type and degree of difficulty of problems assigned. Most problems requiring significant numerical computations can be solved with a personal computer using either POLYMATH or MATLAB.

B. The Goals

B.1. To Develop a Fundamental Understanding of Reaction Engineering

The first goal of this book is to enable the reader to develop a clear understanding of the fundamentals of chemical reaction engineering. This goal will be achieved by presenting a structure that allows the reader to solve reaction engineering problems through reasoning rather than through memorization and recall of numerous equations and the restrictions and conditions under which each equation applies. To accomplish this, we use (1) conventional problems that reinforce the student's understanding of the basic concepts and principles (included at the end of each chapter); (2) problems whose solution requires reading the literature, handbooks, or other textbooks on chemical engineering kinetics; and (3) problems that give students practice in problem

definition and alternative pathways to solutions. The algorithms presented in the text for reactor design provide a framework through which one can develop confidence through reasoning rather than memorization.

To give a reference point as to the level of understanding required in the profession, a number of reaction engineering problems from the *California Board of Registration for Civil and Professional Engineers—Chemical Engineering Examinations* (PECEE) are included. Typically, each problem should require approximately one-half hour to solve. Hints on how to work the California exam problems can be found in the *Summary Notes* and in the *Thoughts on Problem Solving* on the CD-ROM.

The second and third goals of this book are to increase the student's critical thinking skills and creative thinking skills by presenting heuristics and problems that encourage the student to practice these skills.

B.2. To Develop Critical Thinking Skills

Due to the rapid addition of new information and the advancement of science and technology that occur almost daily, an engineer must constantly expand his or her horizons beyond simply gathering information and relying on the basic engineering principles.

A number of homework problems have been included that are designed to enhance critical thinking skills. Socratic questioning is at the heart of critical thinking and a number of homework problems draw from R. W. Paul's six types of Socratic questions:¹

- (1) *Questions for clarification:* Why do you say that? How does this relate to our discussion?
- (2) *Questions that probe assumptions:* What could we assume instead? How can you verify or disprove that assumption?
- (3) *Questions that probe reasons and evidence:* What would be an example?
- (4) *Questions about viewpoints and perspectives:* What would be an alternative?
- (5) *Questions that probe implications and consequences:* What generalizations can you make? What are the consequences of that assumption?
- (6) *Questions about the question:* What was the point of this question? Why do you think I asked this question?

Practice in critical thinking can be achieved by assigning additional parts to the problems at the end of each chapter that utilize R. W. Paul's approach. Most of these problems have more than one part to them. The instructor may wish to assign all or some of the parts. In addition, the instructor could add the following parts to any of the problems:

- Describe how you went about solving this problem.
- How reasonable is each assumption you made in solving this problem?

¹ Paul, R. W., *Critical Thinking* (Published by the Foundation for Critical Thinking, Santa Rosa, CA, 1992).

- Ask another question or suggest another calculation that can be made for this problem.
- Write a few sentences about what you learned from working this homework problem and what you think the point of the problem is.

Another important exercise in this text that fosters critical thinking is the critiquing of journal articles. For the last 20 years, students in the graduate reaction engineering class at the University of Michigan have been required to carry out an in-depth critique of a journal article on chemical engineering kinetics. Although the students were told that choosing an article with erroneous data or reasoning was not necessary for a successful critique, finding an error made the whole assignment much more fun and interesting. Consequently, a select number of problems at the end of chapters involve the critique of journal articles on reaction engineering which may or may not have major or minor inconsistencies. In some cases, a small hint is given to guide the student in his or her analysis.

B.3. To Develop Creative Thinking Skills

To help develop creative thinking skills, a number of problems are open-ended to various degrees. Beginning with Chapter 4, the first problem in each chapter provides students the opportunity to practice their creative skills by making up and solving an original problem. Problem 4-1 gives some guidelines for developing original problems. A number of techniques that can aid the students in practicing their creativity (e.g., lateral thinking and brainstorming) can be found in Fogler and LeBlanc.²

"What if..." problems can serve to develop both critical and creative thinking skills. The second problem of each chapter (e.g., 4-2) contains "What if..." questions that encourage the student to think beyond a single answer or operating condition. These problems can be used in conjunction with the living example problems on the CD to explore the problem. Here, questioning can be carried out by varying the parameters in the problems.

One of the major goals at the undergraduate level is to bring the students to the point where they can solve complex reaction systems, such as multiple reactions with heat effects, and then ask "What if..." questions and look for optimum operating conditions. One problem whose solution exemplifies this goal is the Manufacture of Styrene, **Problem 8-30**.

- | | |
|--|--------------------|
| (1) Ethylbenzene \rightarrow Styrene + Hydrogen: | <i>Endothermic</i> |
| (2) Ethylbenzene \rightarrow Benzene + Ethylene: | <i>Endothermic</i> |
| (3) Ethylbenzene + Hydrogen \rightarrow Toluene + Methane: | <i>Exothermic</i> |

In this problem, the students can find a number of operating conditions which maximize the yield and selectivity.

The parameters can also be easily varied in the example problems by loading the POLYMATH or MATLAB programs from the CD onto a computer to explore and answer "What if..." questions.

² Fogler, H. S. and S. E. LeBlanc, *Strategies for Creative Problem Solving* (Upper Saddle River, NJ: Prentice Hall, 1995).

C. The Structure

The strategy behind the presentation of material is to continually build on a few basic ideas in chemical reaction engineering to solve a wide variety of problems. These ideas are referred to as the *Pillars of Chemical Reaction Engineering*, on which different applications rest. The pillars holding up the application of chemical reaction engineering are shown in Figure P-1.

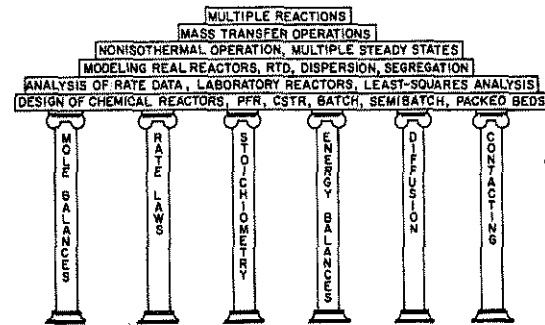


Figure P-1 Pillars of Chemical Reaction Engineering.

The architecture and construction of the structure shown in Figure P-1 had many participants, most notably Professors Amundson, Aris, Smith, Levenspiel, and Denbigh. The contents of this book may be studied in virtually any order after the first four chapters, with few restrictions. A flow diagram showing possible paths is shown in Figure P-2.

In a three-hour undergraduate course at the University of Michigan, approximately eight chapters are covered in the following order: Chapters 1, 2, 3, 4, and 6, Sections 5.1–5.3, and Chapters 8, 10, and parts of either 7 or 13. Complete sample syllabi for a 3-credit-hour course and a 4-credit-hour course can be found on the CD-ROM.

The reader will observe that although metric units are used primarily in this text (e.g., kmol/m^3 , J/mol), a variety of other units are also employed (e.g., lb/ft^3). This is intentional. It is our feeling that whereas most papers published in the future will use the metric system, today's engineers as well as those graduating over the next ten years will be caught in the transition between English, SI, and metric units. As a result, engineers will be faced with extracting information and reaction rate data from older literature which uses English units as well as the current literature using metric units, and they should be equally at ease with both.

The notes in the margins are meant to serve two purposes. First, they act as guides or as commentary as one reads through the material. Second, they identify key equations and relationships that are used to solve chemical reaction engineering problems.

Finally, in addition to developing the intellectual skills discussed above, this is a book for the professional bookshelf. It is a "how to" book with numerous

Margin Notes

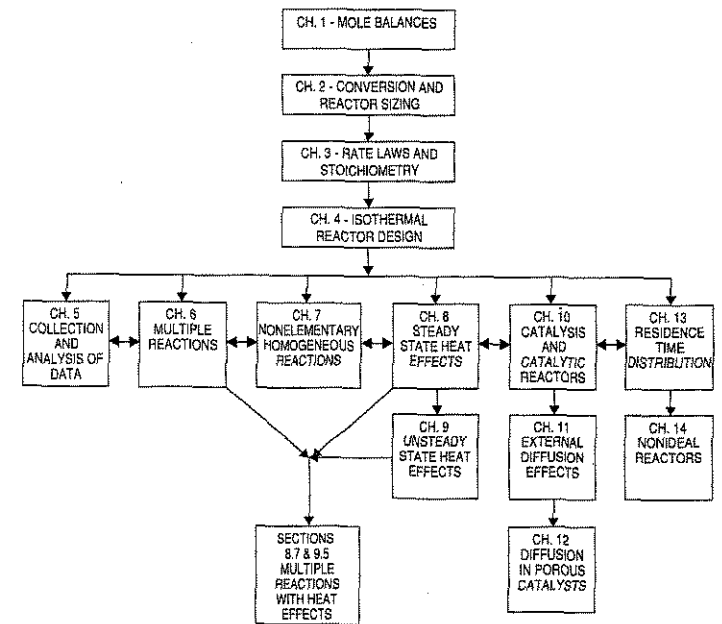


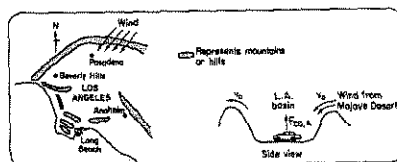
Figure P-2 Sequences for Studying the Text.

examples and clear explanations, rather than an outline of the principles and the *philosophy of chemical reaction engineering*. There are many other applications described in the text.

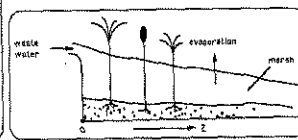
D. The Applications

Important applications of chemical reaction engineering (CRE) of all kinds can be found both inside and outside the chemical process industries (CPI). In this text, examples from the chemical process industries include the manufacture of ethylene oxide, phthalic anhydride, ethylene glycol, metaxylene, styrene, sulfur trioxide, propylene glycol, ketene, and *i*-butane just to name a few. Also, plant safety in the CPI is addressed in both example problems and homework problems. These are real industrial reactions with actual data and reaction rate law parameters.

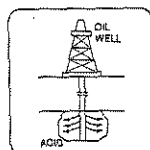
Because of the wide versatility of the principles of CRE, a number of examples outside the CPI are included, such as the use of wetlands to degrade toxic chemicals, smog formation, longevity of motor oils, oil recovery, and pharmacokinetics (cobra bites, SADD-MADD, drug delivery). A sampling of the applications is shown graphically in the following figures.



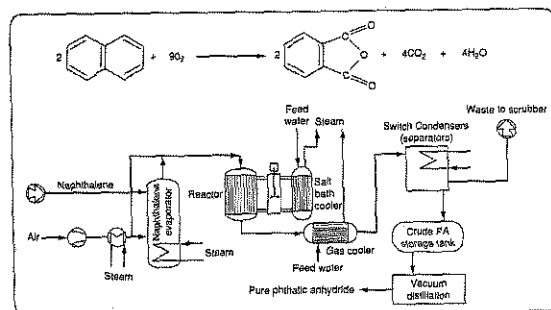
Smog (Ch. 1, Ch. 7)



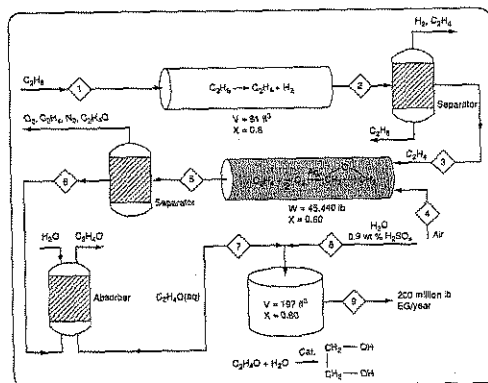
Wetlands (Ch. 4)

Oil Recovery
(Ch. 5)

Cobra Bites (Ch. 6)

Lubricant Design
(Ch. 7)Plant Safety
(Ch. 8 & 9)

Manufacture of Phthalic Anhydride (Ch. 3)



Chemical Plant for Ethylene Glycol using Examples from Ch. 4

E. The Components of the CD-ROM

The primary purpose of the CD-ROM is to serve as an enrichment resource. Its objectives are fourfold: (1) To provide the option/opportunity for further study or clarification on a particular concept or topic through Summary Notes, additional examples, interactive computing modules and web modules, (2) To provide the opportunity to practice critical thinking skills, creative thinking skills, and problem solving skills through the use of "What if..." questions and "living example problems," (3) To provide additional technical material for the professional reference shelf, (4) To provide other tutorial information, such as additional homework problems, thoughts on problem solving, how to use computational software in chemical reaction engineering, and representative course structures. The following components are listed at the end of most chapters and can be accessed, by chapter, on the CD.

• Learning Resources

These resources give an overview of the material in each chapter and provide extra explanations, examples, and applications to reinforce the basic concepts of chemical reaction engineering. The learning resources on the CD-ROM include:

1. Summary Notes

These are Summary Notes that will give an overview of each chapter, and are taken from lecture notes from an undergraduate class at Michigan.

2. Web Modules

These modules which apply key concepts to both standard and non-standard reaction engineering problems (e.g., the use of wetlands to degrade toxic chemicals, cobra bites) can be loaded directly from the CD-ROM. Additional Web Modules are expected to be added over the next several years. (<http://www.engin.umich.edu/~cre>)

3. Interactive Computer Modules

Students can use the corresponding Interactive Computer Modules to review the important chapter concepts and then apply them to real problems in a unique and entertaining fashion. The Murder Mystery module has long been a favorite with students across the nation.

4. Solved Problems

A number of solved problems are presented along with problem-solving heuristics. Problem-solving strategies and additional worked example problems are available in the **Thoughts on Problem Solving** section of the CD-ROM.

• Living Example Problems

A copy of POLYMATH is provided on the CD-ROM for the students to use to solve the homework problems. The example problems that use an ODE solver (e.g., POLYMATH) are referred to as "living example problems" because the students can load the POLYMATH program directly onto their own computer in order to study the problem. Stu-

dents are encouraged to change parameter values and to "play with" the key variables and assumptions. Using the living example problems to explore the problem and asking "What if..." questions provides the opportunity to practice critical and creative thinking skills.

- **Professional Reference Shelf**

This section of the CD-ROM contains:

1. material that is important to the practicing engineer, although it is typically not included in the majority of chemical reaction engineering courses.
2. material that gives a more detailed explanation of derivations that were abbreviated in the text. The intermediate steps to these derivations are given on the CD-ROM.

- **Additional Homework Problems**

New problems were developed for this edition that provide a greater opportunity to use today's computing power to solve realistic problems.

- **Other CD-ROM Material**

In addition to the components listed at the end of each chapter the following components are included on the CD-ROM:

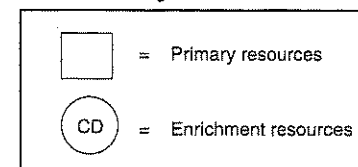
1. *Software ToolBox*
Instructions on how to use the different software packages (POLY-MATH, MATLAB, and ASPEN PLUS) to solve examples.
2. *Representative Syllabi for a 3- and a 4-Credit Course*
The syllabi give a sample pace at which the course could be taught as well as suggested homework problems.
3. *FAQ*
These are Frequently Asked Questions (FAQ's) from undergraduate students taking reaction engineering.

- **Virtual Reality Module (WWW)**

This module provides an opportunity to move inside a catalyst pellet to observe surface reactions and coking. It can be found at <http://www.engin.umich.edu/labs/vrichel>.

F. The Integration of the Text and the CD-ROM

There are a number of ways one can use the CD in conjunction with the text. The CD provides *enrichment resources* for the reader in the form of interactive tutorials. Pathways on how to use the materials to learn chemical reaction engineering are shown in Figure P-3 and P-4. The keys to the CRE learning flowsheets are



F.1. For the University Student

In developing a fundamental understanding of the material, the student may wish to use only the primary resources without using the CD-ROM, (i.e., using only the boxes shown in Figure P-3) or the student may use a few or all of the interactive tutorials in the CD-ROM (i.e., the circles shown in Figure P-3). However, to practice the skills that enhance critical and creative thinking, the students are strongly encouraged to use the *Living Example Problems* and vary the model parameters to ask and answer "What if..." questions.

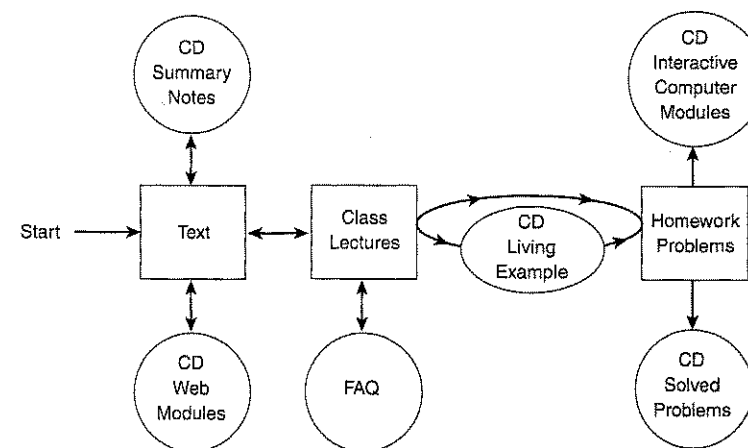


Figure P-3 A Student Pathway to Integrate the Class Text and CD.

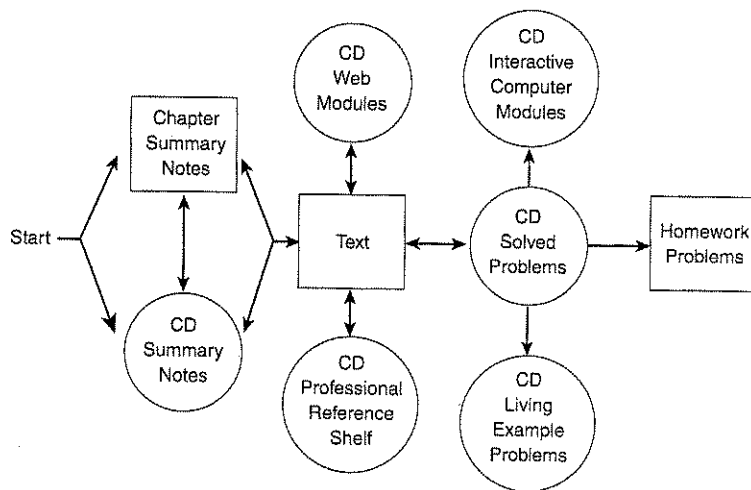


Figure P-4 A Problem-Solving Pathway to Integrate the text and the CD.

One notes that while the author recommends studying the living examples before working home problems, they may be bypassed, as is the case with all the enrichment resources if time is not available. However, class testing of the enrichment resources reveals that they not only greatly aid in learning the material but they may also serve to motivate students through the novel use of CRE principles.

F.2. For the Practicing Engineer

Practicing engineers may want to first review the CD summary notes or the summaries at the end of each chapter to refresh their memories as to what they have previously studied. They can then focus on the topics that they want to study in the text using the web modules, solved problems, and interactive computer modules as tutorials. They can also learn more about specialty topics by using the CD reference shelf. The flow diagram is shown in Figure P-4.

G. The Web

The Web site (<http://www.engin.umich.edu/~cre>) will be used to update the text and the CD-ROM. It will identify typographical and other errors in the 1st and 2nd printings of the 3rd edition of the text. In the near future, additional material will be added to include more solved problems as well as additional Web Modules.

H. What's New

The main thrust of the new edition is to enable the student to solve *Digital Age*³ reaction engineering problems. Consequently the content, example problems, and homework problems focus on achieving this goal. These problems provide the students an opportunity to practice their critical and creative thinking skills by "playing with" the problems through parameter variations. Consequently, some of the text material, e.g., control of chemical reactors and safety, was added because it provides opportunities to formulate and solve problems. For example, in the *Case Study* on safety, the student can use the CD-ROM to carry out a post-mortem on the nitroaniline explosion in Example 9-2 to find out what would have happened if the cooling had failed for 5 minutes instead of 10 minutes. Significant effort has been devoted to developing example and homework problems that foster critical and creative thinking.

The use of mole balances in terms of concentrations and flow rates rather than conversions is introduced early in the text so they can be easily applied to membrane reactors and multiple reactions. The 3rd edition contains more industrial chemistry with real reactors and real reactions and extends the wide range of applications to which chemical reaction engineering principles can be applied (i.e., cobra bites, drug medication, ecological engineering). New material includes spherical reactors, recycle reactors, trickle bed reactors, fluidized bed reactors, regression of rate data, etching of semiconductors, multiple reactions in RTD models, the application of process control to CSTRs, safety, collision theory, transition state theory, and an example using computational chemistry to calculate an activation energy. The material that has been greatly expanded includes polymerization, heat effects in batch reactors and in multiple reactions, catalysts and catalytic reactions, experimental design, and reactor staging. The living example problems on the CD-ROM are in both POLY-MATH and MATLAB.

A large number of enrichment resources are provided on the CD-ROM that can help the student over difficult spots. However, if there is a time constraint, or the reader's computer breaks down, the reader need only read the text and proceed along the pathway of the boxes shown in Figures P-3 and P-4.

I. Acknowledgments

Many of the problems at the end of the various chapters were selected from the *California Board of Registration for Civil and Professional Engineers—Chemical Engineering Examinations (PECEE)* in past years. The permission for use of these problems, which, incidentally, may be obtained from the Documents Section, California Board of Registration for Civil and Professional Engineers—Chemical Engineering, 1004 6th Street, Sacramento, CA 95814, is gratefully acknowledged. (Note: These problems have been copyrighted by the California Board of Registration and may not be reproduced without their permission.)

³ Fogler, H. S., "Teaching Critical Thinking, Creative Thinking, and Problem Solving in the Digital Age" (Phillips Lecture, Oklahoma State University Press, April 25, 1997).

However, all intensive laws tend often to have exceptions. Very interesting concepts take orderly, responsible statements. Virtually all laws intrinsically are natural thoughts. General observations become laws under experimentation.

There are so many colleagues and students who contributed to this book that it would require another chapter to thank them all in an appropriate manner.

I would like to again acknowledge all my friends and colleagues for their contributions to the 1st and 2nd editions (See Introduction, CD-ROM). For the 3rd edition, I would like to give special recognition to the students who contributed so much to the CD-ROM: In particular, Dieter Schweiss, Anuj Hasija, Jim Piana, and Susan Fugett, with thanks also to Anurag Murial, Gavin Sy, Scott Conaway, Mayur Valanju, Matt Robinson, Tim Mashue, Lisa Ingalls, Sean Conners, Gustavo Bolaños, and Ellyne Buckingham. Further, Tim Hubbard, Jessica Hamman, David Johnson, Kylas Subramanian, Sumate Charoenchaidet, Lisa Ingalls, Probjot Singh, Abe Sendijarevic, and Nicholas R. Abu-Absi worked on the solution manual. Jason Ferns, Rob Drewitt, and Probjot Singh contributed to the problems, while Professor Andy Hrymak, Probjot Singh, Marty Johnson, Sumate Charoenchaidet, N. Vijay, and K. Subramanian helped with proofreading the galleys. Thanks to my graduate students Venkat Ramachandran, Chris Fredd, Dong Kim, Barry Wolf, Probjot Singh, Vaibhav Nalwaya, and Ann Wattana for their patience and understanding. Barbara Zieder (copy-editing), Lisa Garboski (production), and Yvette Raven (CD-ROM) did an excellent job in bringing the project to a successful completion. Bernard Goodwin of Prentice Hall was extremely helpful and supportive throughout. The stimulating discussions with Professors John Falconer, D. B. Battacharia, Richard Braatz, Kristi Anseth, and Al Weimer are greatly appreciated. I also appreciate the friendship and insights provided by Dr. Lee Brown, who contributed to chapters 8, 12, 13, and 14. Professor Mike Cutlip gave not only suggestions and a critical reading of many sections, but most important provided continuous support and encouragement throughout the course of this project. Laura Bracken is so much a part of this manuscript through her excellent deciphering of equations and scribbles, and typing, her organization, and always present wonderful disposition. Thanks *Radar*!! Finally, to my wife Janet, love and thanks. Without her enormous help and support the project would not have been possible.

HSF
Ann Arbor

*Elements
of Chemical
Reaction
Engineering*

Third Edition

For updates on the CD and typographical errors for this printing see the web site:

<http://www.engin.umich.edu/~cre>

Mole Balances

1

The first step to knowledge
is to know that we are ignorant.

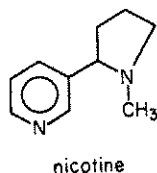
Socrates (470–399 B.C.)

Chemical kinetics and reactor design are at the heart of producing almost all industrial chemicals. It is primarily a knowledge of chemical kinetics and reactor design that distinguishes the chemical engineer from other engineers. The selection of a reaction system that operates in the safest and most efficient manner can be the key to the economic success or failure of a chemical plant. For example, if a reaction system produced a large amount of undesirable product, subsequent purification and separation of the desired product could make the entire process economically unfeasible. The chemical kinetic principles learned here, in addition to the production of chemicals, can be applied in areas such as living systems, waste treatment, and air and water pollution. Some of the examples and problems used to illustrate the principles of chemical reaction engineering are: the use of wetlands to remove toxic chemicals from rivers, increasing the octane number of gasoline, the production of anti-freeze starting from ethane, the manufacture of computer chips, and the application of enzyme kinetics to improve an artificial kidney.

This book focuses on a variety of chemical reaction engineering topics. It is concerned with the rate at which chemical reactions take place, together with the mechanism and rate-limiting steps that control the reaction process. The sizing of chemical reactors to achieve production goals is an important segment. How materials behave within reactors, both chemically and physically, is significant to the designer of a chemical process, as is how the data from chemical reactors should be recorded, processed, and interpreted.

Before entering into discussions of the conditions that affect chemical reaction rates and reactor design, it is necessary to account for the various chemical species entering and leaving a reaction system. This accounting process is achieved through overall mole balances on individual species in the

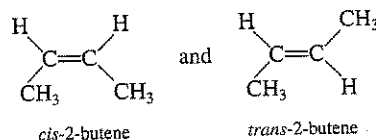
reacting system. In this chapter we develop a general mole balance that can be applied to any species (usually a chemical compound) entering, leaving, and/or remaining within the reaction system volume. After defining the rate of reaction, $-r_A$, and discussing the earlier difficulties of properly defining the chemical reaction rate, in this chapter we show how the general balance equation may be used to develop a preliminary form of the design equations of the most common industrial reactors: batch, continuous-stirred tank (CSTR), and tubular. In developing these equations, the assumptions pertaining to the modeling of each type of reactor are delineated. Finally, a brief summary and series of short review questions are given at the end of the chapter.



1.1 Definition of the Rate of Reaction, $-r_A$

We begin our study by performing mole balances on each chemical species in the system. Here, the term *chemical species* refers to any chemical compound or element with a given identity. The identity of a chemical species is determined by the *kind*, *number*, and *configuration* of that species' atoms. For example, the species nicotine (a bad tobacco alkaloid) is made up of a fixed number of specific elements in a definite molecular arrangement or configuration. The structure shown illustrates the kind, number, and configuration of the species nicotine (responsible for "nicotine fits") on a molecular level.

Even though two chemical compounds have exactly the same number of atoms of each element, they could still be different species because of different configurations. For example, 2-butene has four carbon atoms and eight hydrogen atoms; however, the atoms in this compound can form two different arrangements.



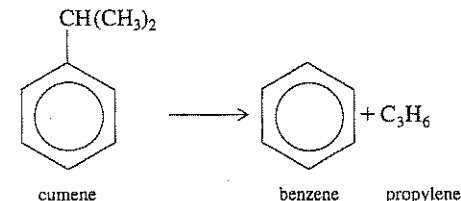
As a consequence of the different configurations, these two isomers display different chemical and physical properties. Therefore, we consider them as two different species even though each has the same number of atoms of each element.

We say that a *chemical reaction* has taken place when a detectable number of molecules of one or more species have lost their identity and assumed a new form by a change in the kind or number of atoms in the compound and/or by a change in structure or configuration of these atoms. In this classical approach to chemical change, it is assumed that the total mass is neither created nor destroyed when a chemical reaction occurs. The mass referred to is the total collective mass of all the different species in the system. However, when considering the individual species involved in a particular reaction, we do speak of the rate of disappearance of mass of a particular species. The rate of disappearance of a species, say species A, is the number of A molecules that

When has a chemical reaction taken place?

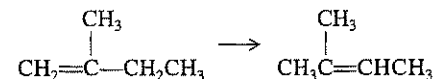
lose their chemical identity per unit time per unit volume through the breaking and subsequent re-forming of chemical bonds during the course of the reaction. In order for a particular species to "appear" in the system, some prescribed fraction of another species must lose its chemical identity.

There are three basic ways a species may lose its chemical identity. One way is by *decomposition*, in which a molecule is broken down into smaller molecules, atoms, or atom fragments. For example, if benzene and propylene are formed from a cumene molecule,



the cumene molecule has lost its identity (i.e., disappeared) by breaking its bonds to form these molecules. A second way that a molecule may lose its species identity is through *combination* with another molecule or atom. In the example above, the propylene molecule would lose its species identity if the reaction were carried out in the reverse direction so that it combined with benzene to form cumene.

The third way a species may lose its identity is through *isomerization*, such as the reaction

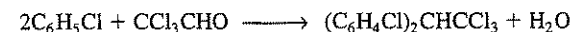


A species can lose its identity by decomposition, combination, or isomerization

Here, although the molecule neither adds other molecules to itself nor breaks into smaller molecules, it still loses its identity through a change in configuration.

To summarize this point, we say that a given number of molecules (e.g., mole) of a particular chemical species have reacted or disappeared when the molecules have lost their chemical identity.

The rate at which a given chemical reaction proceeds can be expressed in several ways. It can be expressed either as the rate of disappearance of reactants or the rate of formation of products. For example, the insecticide DDT (dichlorodiphenyltrichloroethane) is produced from chlorobenzene and chloral in the presence of fuming sulfuric acid.



What is $-r_A$?
 r_A ?

Letting the symbol A represent the chemical chloral, the numerical value of the **rate of reaction**, $-r_A$, is defined as the *number of moles of chloral reacting (disappearing) per unit time per unit volume* ($\text{mol}/\text{dm}^3 \cdot \text{s}$). In the next chapter we delineate the prescribed relationship between the rate of formation of one

species, r_j (e.g., DDT), and the rate of disappearance of another species, $-r_i$ (e.g., chlorobenzene), in a chemical reaction.

In heterogeneous reaction systems, the rate of reaction is usually expressed in measures other than volume, such as reaction surface area or catalyst weight. Thus for a gas-solid catalytic reaction, the dimensions of this rate, $-r_A$, are the number of moles of A reacted per unit time per unit mass of catalyst (mol/s · g catalyst). Most of the introductory discussions on chemical reaction engineering in this book focus on homogeneous systems.

The mathematical definition of a chemical reaction rate has been a source of confusion in chemical and chemical engineering literature for many years. The origin of this confusion stems from laboratory bench-scale experiments that were carried out to obtain chemical reaction rate data. These early experiments were batch-type, in which the reaction vessel was closed and rigid; consequently, the ensuing reaction took place at constant volume. The reactants were mixed together at time $t = 0$ and the concentration of one of the reactants, C_A , was measured at various times t . The rate of reaction was determined from the slope of a plot of C_A as a function of time. Letting r_A be the rate of formation of A per unit volume (e.g., g mol/s · dm³), the investigators then defined and reported the chemical reaction rate as

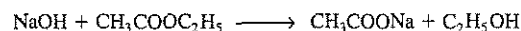
$$r_A = \frac{dC_A}{dt} \quad (1-1)$$

However, this definition was for a *constant-volume batch reactor*.

As a result of the limitations and restrictions given, Equation (1-1) is a rather limited and confusing definition of the chemical reaction rate. For amplification of this point, consider the following steady-flow system in which the saponification of ethyl acetate is carried out.

Example 1-1 Is Sodium Hydroxide Reacting?

Sodium hydroxide and ethyl acetate are continuously fed to a rapidly stirred tank in which they react to form sodium acetate and ethanol:



(Figure E1-1.1). The product stream, containing sodium acetate and ethanol, together with the unreacted sodium hydroxide and ethyl acetate, is continuously withdrawn from the tank at a rate equal to the total feed rate. The contents of the tank in which this reaction is taking place may be considered to be perfectly mixed. Because the system is operated at steady state, if we were to withdraw liquid samples at some location in the tank at various times and analyze them chemically, we would find that the concentrations of the individual species in the different samples were identical. That is, the concentration of the sample taken at 1 P.M. is the same as that of the sample taken at 3 P.M. Because the species concentrations are constant and therefore do not change with time,

$$\frac{dC_A}{dt} = 0 \quad (\text{E1-1.1})$$

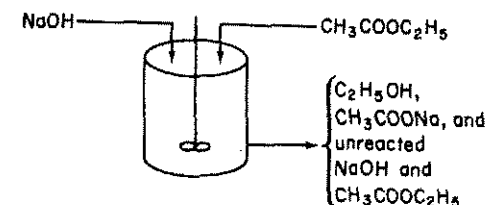


Figure E1-1.1 Well mixed reaction vessel.

where $A \equiv \text{NaOH}$. Substitution of Equation (E1-1.1) into Equation (1-1) leads to

$$r_A = 0 \quad (\text{E1-1.2})$$

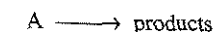
which is incorrect because $\text{C}_2\text{H}_5\text{OH}$ and CH_3COONa are being formed from NaOH and $\text{CH}_3\text{COOC}_2\text{H}_5$ at a finite rate. Consequently, the rate of reaction as defined by Equation (1-1) cannot apply to a flow system and is incorrect if it is defined in this manner.

Definition of r_j

By now you should be convinced that Equation (1-1) is not the definition of the chemical reaction rate. We shall simply say that r_j is the rate of formation of species j per unit volume. It is the number of moles of species j generated per unit volume per unit time. The rate equation for r_j is solely a function of the properties of the reacting materials [e.g., species concentration (i.e. activities), temperature, pressure, or type of catalyst, if any] at a point in the system and is independent of the type of system (i.e., batch or continuous flow) in which the reaction is carried out. However, since the properties of the reacting materials can vary with position in a chemical reactor, r_j can in turn be a function of position and can vary from point to point in the system.

What is $-r_A$ a function of?

The chemical reaction rate is an intensive quantity and depends on temperature and concentration. The reaction rate equation (i.e., the rate law) is essentially an algebraic equation involving concentration, not a differential equation.¹ For example, the algebraic form of the rate law $-r_A$ for the reaction



may be a linear function of concentration,

$$-r_A = kC_A$$

or it may be some other algebraic function of concentration, such as

¹ For further elaboration on this point, see *Chem. Eng. Sci.*, 25, 337 (1970); B. L. Crynes and H. S. Fogler, eds., *AIChE Modular Instruction Series E: Kinetics*, Vol. 1 (New York: AIChE, 1981), p. 1; and R. L. Kabel, "Rates," *Chem. Eng. Commun.*, 9, 15 (1981).

$$-r_A = kC_A^2 \quad (1-2)$$

or

$$-r_A = \frac{k_1 C_A}{1 + k_2 C_A}$$

The rate law is an algebraic equation

For a given reaction, the particular concentration dependence that the rate law follows (i.e., $-r_A = kC_A$ or $-r_A = kC_A^2$ or ...) must be determined from experimental observation. Equation (1-2) states that the rate of disappearance of A is equal to a rate constant k times the square of the concentration of A. By convention, r_A is the rate of formation of A; consequently, $-r_A$ is the rate of disappearance of A. Throughout this book the phrase *rate of generation* means exactly the same as the phrase *rate of formation*, and these phrases are used interchangeably.

1.2 The General Mole Balance Equation

To perform a mole balance on any system, the system boundaries must first be specified. The volume enclosed by these boundaries will be referred to as the *system volume*. We shall perform a mole balance on species j in a system volume, where species j represents the particular chemical species of interest, such as water or NaOH (Figure 1-1).

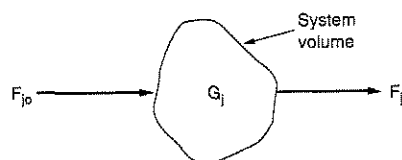


Figure 1-1 Balance on system volume.

A mole balance on species j at any instant in time, t , yields the following equation:

	$\left[\begin{array}{c} \text{rate of flow} \\ \text{of } j \text{ into} \\ \text{the system} \\ \text{(moles/time)} \end{array} \right] + \left[\begin{array}{c} \text{rate of generation} \\ \text{of } j \text{ by chemical} \\ \text{reaction within} \\ \text{the system} \\ \text{(moles/time)} \end{array} \right] - \left[\begin{array}{c} \text{rate of flow} \\ \text{of } j \text{ out of} \\ \text{the system} \\ \text{(moles/time)} \end{array} \right] = \left[\begin{array}{c} \text{rate of} \\ \text{accumulation} \\ \text{of } j \text{ within} \\ \text{the system} \\ \text{(moles/time)} \end{array} \right]$	
Mole balance	$F_{j0} + G_j - F_j = \frac{dN_j}{dt} \quad (1-3)$	
in	+ generation	- out = accumulation

where N_j represents the number of moles of species j in the system at time t . If all the system variables (e.g., temperature, catalytic activity, concentration of

the chemical species) are spatially uniform throughout the system volume, the rate of generation of species j , G_j , is just the product of the reaction volume, V , and the rate of formation of species j , r_j .

$$G_j = r_j \cdot V$$

$$\frac{\text{moles}}{\text{time}} = \frac{\text{moles}}{\text{time} \cdot \text{volume}} \cdot \text{volume}$$

Suppose now that the rate of formation of species j for the reaction varies with the position in the system volume. That is, it has a value r_{j1} at location 1, which is surrounded by a small volume, ΔV_1 , within which the rate is uniform; similarly, the reaction rate has a value r_{j2} at location 2 and an associated volume, ΔV_2 (Figure 1-2). The rate of generation, ΔG_{j1} , in terms of r_{j1} and

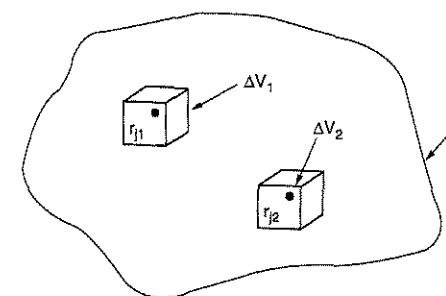


Figure 1-2 Dividing up the system volume V .

subvolume ΔV_1 is

$$\Delta G_{j1} = r_{j1} \Delta V_1$$

Similar expressions can be written for ΔG_{j2} and the other system subvolumes ΔV_i . The total rate of generation within the system volume is the sum of all the rates of generation in each of the subvolumes. If the total system volume is divided into M subvolumes, the total rate of generation is

$$G_j = \sum_{i=1}^M \Delta G_{ji} = \sum_{i=1}^M r_{ji} \Delta V_i$$

By taking the appropriate limits (i.e., let $M \rightarrow \infty$ and $\Delta V \rightarrow 0$) and making use of the definition of an integral, we can rewrite the foregoing equation in the form

$$G_j = \int_V r_j dV$$

From this equation we see that r_j will be an indirect function of position, since the properties of the reacting materials (e.g., concentration, temperature) can have different values at different locations in the reactor.

We now replace G_j in Equation (1-3),

$$F_{j0} - F_j + G_j = \frac{dN_j}{dt}$$

by its integral form to yield a form of the general mole balance equation for any chemical species j that is entering, leaving, reacting, and/or accumulating within any system volume V .

$$F_{j0} - F_j + \int_V r_j dV = \frac{dN_j}{dt} \quad (1-4)$$

This is a basic equation for chemical reaction engineering

From this general mole balance equation we can develop the design equations for the various types of industrial reactors: batch, semibatch, and continuous-flow. Upon evaluation of these equations we can determine the time (batch) or reactor volume (continuous-flow) necessary to convert a specified amount of the reactants to products.

1.3 Batch Reactors

A batch reactor has neither inflow nor outflow of reactants or products while the reaction is being carried out; $F_{j0} = F_j = 0$. The resulting general mole balance on species j is

$$\frac{dN_j}{dt} = \int_V r_j dV$$

If the reaction mixture is perfectly mixed so that there is no variation in the rate of reaction throughout the reactor volume, we can take r_j out of the integral and write the mole balance in the form

$$\frac{dN_j}{dt} = r_j V \quad (1-5)$$

Figure 1-3 shows two different types of batch reactors used for gas-phase reactions. Reactor A is a constant-volume (variable-pressure) reactor and Reactor B is a constant-pressure (variable-volume) reactor. At time $t = 0$, the reactants are injected into the reactor and the reaction is initiated. To see clearly the different forms the mole balance will take for each type of reactor, consider the following examples, in which the gas-phase decomposition of dimethyl ether is taking place to form methane, hydrogen, and carbon monoxide:

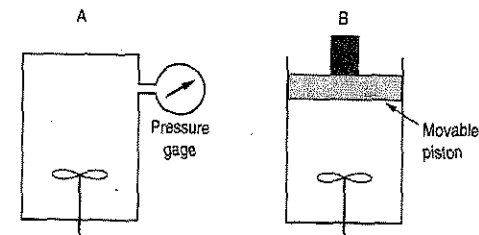
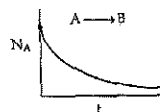
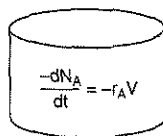
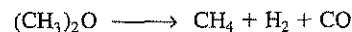


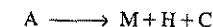
Figure 1-3 Batch reactors for gas-phase reactions.

Example 1-2 Constant Volume or Constant Pressure: Does It Make a Difference?

Write the mole balance for dimethyl ether in terms of the reactor volume, concentration, and rate of formation of dimethyl ether for both a constant-pressure and a constant-volume batch reactor.

Solution

To reduce the number of subscripts, we write the reaction symbolically as



where A is dimethyl ether, M is methane, H is hydrogen, and C is carbon monoxide. For both batch reactors, the mole balance on A is

$$\frac{1}{V} \frac{dN_A}{dt} = r_A \quad (1-5)$$

In writing the mole balance for dimethyl ether for a batch reactor, the only assumption made is that there are no spatial variations in r_A .

Constant-volume batch reactor. The reactor is perfectly mixed so that the concentration of the reacting species is spatially uniform. Because the volume is constant we can take V inside the differential and write the mole balance in terms of the concentration of A:

$$\frac{1}{V} \frac{dN_A}{dt} = \frac{d(N_A/V)}{dt} = \frac{dC_A}{dt} = r_A \quad (\text{E1-2.1})$$

Constant-pressure batch reactor. To write the mole balance for this reactor in terms of concentration, we again use the fact that

$$N_A = C_A V$$

$$\frac{1}{V} \frac{dN_A}{dt} = \frac{1}{V} \frac{d(C_A V)}{dt} = \frac{dC_A}{dt} + \frac{C_A}{V} \frac{dV}{dt} = r_A \quad (\text{E1-2.2})$$

$$r_A = \frac{dC_A}{dt} + \frac{C_A}{V} \frac{dV}{dt} \quad (\text{E1-2.3})$$

The difference between equations (E1-2.1) and (E1-2.3) for the two different types of reactors is apparent.

1.4 Continuous-Flow Reactors

1.4.1 Continuous-Stirred Tank Reactor

A type of reactor used very commonly in industrial processing is a stirred tank operated continuously (Figure 1-4). It is referred to as the *continuous-stirred tank reactor* (CSTR) or *backmix reactor*. The CSTR is normally run at steady state and is usually operated so as to be quite well mixed. As a result of the latter quality, the CSTR is generally modeled as having no spatial variations in concentration, temperature, or reaction rate throughout the vessel. Since the temperature and concentration are identical everywhere within the reaction vessel, they are the same at the exit point as they are elsewhere in the tank. Thus the temperature and concentration in the exit stream are modeled as being the same as those inside the reactor. In systems where mixing is highly nonideal, the well-mixed model is inadequate and we must resort to other modeling techniques, such as residence-time distributions, to obtain meaningful results. This topic is discussed in Chapters 13 and 14.

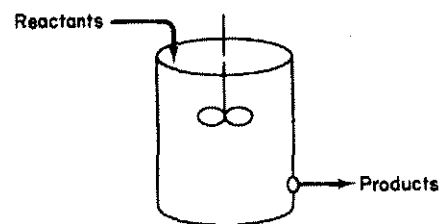


Figure 1-4 Continuous-stirred tank reactor.

When the general mole balance equation

$$F_{j0} - F_j + \int_V r_j dV = \frac{dN_j}{dt} \quad (1-4)$$

is applied to a CSTR operated at steady state (i.e., conditions do not change with time),

$$\frac{dN_j}{dt} = 0$$

in which there are no spatial variations in the rate of reaction,

$$\int_V r_j dV = V r_j$$

it takes the familiar form known as the *design equation* for a CSTR:

$$V = \frac{F_{j0} - F_j}{-r_j} \quad (1-6)$$

The CSTR design equation gives the reactor volume necessary to reduce the entering flow rate of species j , F_{j0} , to the exit flow rate F_j . We note that the CSTR is modeled such that the conditions in the exit stream (e.g., concentration, temperature) are identical to those in the tank. The molar flow rate F_j is just the product of the concentration of species j and the volumetric flow rate v :

$$F_j = C_j \cdot v$$

$$\frac{\text{moles}}{\text{time}} = \frac{\text{moles}}{\text{volume}} \cdot \frac{\text{volume}}{\text{time}} \quad (1-7)$$

1.4.2 Tubular Reactor

In addition to the CSTR and batch reactors, another type of reactor commonly used in industry is the *tubular reactor*. It consists of a cylindrical pipe and is normally operated at steady state, as is the CSTR. For the purposes of the material presented here, we consider systems in which the flow is highly turbulent and the flow field may be modeled by that of plug flow. That is, there is no radial variation in concentration and the reactor is referred to as a plug-flow reactor (PFR). (The laminar flow reactor is discussed in Chapter 13.)

In the tubular reactor, the reactants are continually consumed as they flow down the length of the reactor. In modeling the tubular reactor, we assume that the concentration varies continuously in the axial direction through the reactor. Consequently, the reaction rate, which is a function of concentration for all but zero-order reactions, will also vary axially. The general mole balance equation is given by Equation (1-4):

$$F_{j0} - F_j + \int_V r_j dV = \frac{dN_j}{dt} \quad (1-4)$$

To develop the PFR design equation we shall divide (conceptually) the reactor into a number of subvolumes so that within each subvolume ΔV , the reaction rate may be considered spatially uniform (Figure 1-5). We now focus our attention on the subvolume that is located a distance y from the entrance of the reactor. We let $F_j(y)$ represent the molar flow rate of species j into volume ΔV at y and $F_j(y + \Delta y)$ the molar flow of species j out of the volume at the location $(y + \Delta y)$. In a spatially uniform subvolume ΔV ,

$$\int_V r_j dV = r_j \Delta V$$

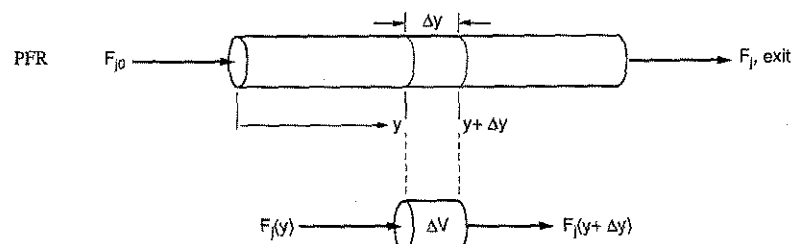


Figure 1-5 Tubular reactor.

For a tubular reactor operated at steady state,

$$\frac{dN_j}{dt} = 0$$

Equation (1-4) becomes

$$F_j(y) - F_j(y + \Delta y) + r_j \Delta V = 0 \quad (1-8)$$

In this expression r_j is an indirect function of y . That is, r_j is a function of reactant concentration, which is a function of the position y down the reactor. The volume ΔV is the product of the cross-sectional area A of the reactor and the reactor length Δy .

$$\Delta V = A \Delta y$$

We now substitute in Equation (1-8) for ΔV and then divide by Δy to obtain

$$-\left[\frac{F_j(y + \Delta y) - F_j(y)}{\Delta y} \right] = -Ar_j$$

The term in brackets resembles the definition of the derivative

$$\lim_{\Delta x \rightarrow 0} \left[\frac{f(x + \Delta x) - f(x)}{\Delta x} \right] = \frac{df}{dx}$$

Taking the limit as Δy approaches zero, we obtain

$$-\frac{dF_j}{dy} = -Ar_j$$

or dividing by -1 , we have

$$\frac{dF_j}{dy} = Ar_j \quad (1-9)$$

It is usually most convenient to have the reactor volume V rather than the reactor length y as the independent variable. Accordingly, we shall change variables using the relation $dV = A dy$ to obtain one form of the design equation for a tubular reactor:

$$\frac{dF_j}{dV} = r_j \quad (1-10)$$

We also note that for a reactor in which the cross-sectional area A varies along the length of the reactor, the design equation remains unchanged. This equation can be generalized for the reactor shown in Figure 1-6, in a manner simi-

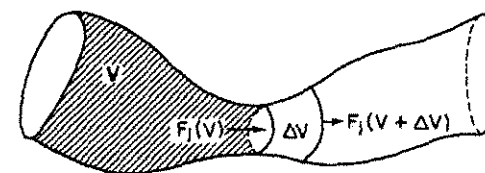


Figure 1-6

lar to that presented above, by utilizing the volume coordinate V rather than a linear coordinate y . After passing through volume V , species j enters subvolume ΔV at volume V at a molar flow rate $F_j(V)$. Species j leaves subvolume ΔV at volume $(V + \Delta V)$, at a molar flow rate $F_j(V + \Delta V)$. As before, ΔV is chosen small enough so that there is no spatial variation of reaction rate within the subvolume:

$$G_j = \int_{\Delta V} r_j dV = r_j \Delta V \quad (1-11)$$

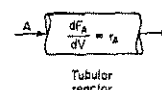
After accounting for steady-state operation in Equation (1-4), it is combined with Equation (1-11) to yield

$$F_j(V) - F_j(V + \Delta V) + r_j \Delta V = 0$$

Rearranging gives

$$\frac{F_j(V + \Delta V) - F_j(V)}{\Delta V} = r_j$$

and taking the limit as $\Delta V \rightarrow 0$, we again obtain Equation (1-10):



$$\frac{dF_j}{dV} = r_j$$

(1-10)

Consequently, we see that Equation (1-10) applies equally well to our model of tubular reactors of variable and constant cross-sectional area, although it is

doubtful that one would find a reactor of the shape shown in Figure 1-6, unless designed by Pablo Picasso. The conclusion drawn from the application of the design equation is an important one: The extent of reaction achieved in a plug-flow tubular reactor (PFR) does not depend on its shape, only on its total volume.

1.4.3 Packed-Bed Reactor

The principal difference between reactor design calculations involving homogeneous reactions and those involving fluid-solid heterogeneous reactions is that for the latter, the reaction rate is based on mass of solid catalyst, W , rather than on reactor volume, V . For a fluid-solid heterogeneous system, the rate of reaction of a substance A is defined as

$$-r'_A = \text{g mol A reacted/s} \cdot \text{g catalyst}$$

The mass of solid is used because the amount of the catalyst is what is important to the rate of reaction. The reactor volume that contains the catalyst is of secondary significance.

In the three idealized types of reactors just discussed [the perfectly mixed batch reactor, the plug-flow tubular reactor, and the perfectly mixed continuous-stirred tank reactor (CSTR)], the design equations (i.e., mole balances) were developed based on reactor volume. The derivation of the design equation for a packed-bed catalytic reactor will be carried out in a manner analogous to the development of the tubular design equation. To accomplish this derivation, we simply replace the volume coordinate in Equation (1-8) with the catalyst weight coordinate W (Figure 1-7). As with the PFR, the PBR is assumed to have

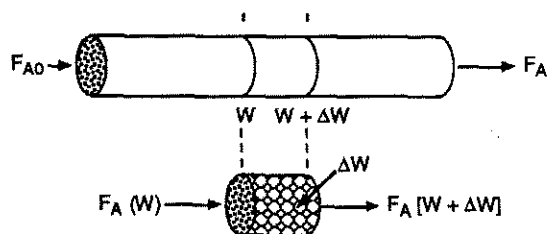


Figure 1-7 Packed-bed reactor schematic.

no radial gradients in concentration, temperature, or reaction rate. The generalized mole balance on species A over catalyst weight ΔW results in the equation

$$\begin{array}{ccccccc} \text{in} & - & \text{out} & + & \text{generation} & = & \text{accumulation} \\ F_A(W) & - & F_A(W + \Delta W) & + & r'_A \Delta W & = & 0 \end{array} \quad (1-12)$$

The dimensions of the generation term in Equation (1-12) are

$$(r'_A) \Delta W = \frac{\text{moles A}}{(\text{time})(\text{mass of catalyst})} \cdot (\text{mass of catalyst}) = \frac{\text{moles A}}{\text{time}}$$

which are, as expected, the same dimension of the molar flow rate F_A . After dividing by ΔW and taking the limit as $\Delta W \rightarrow 0$, we arrive at the differential form of the mole balance for a packed-bed reactor:

$$\frac{dF_A}{dW} = r'_A \quad (1-13)$$

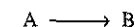
When pressure drop through the reactor (see Section 4.4) and catalyst decay (see Section 10.7) are neglected, the integral form of the packed-catalyst-bed design equation can be used to calculate the catalyst weight.

$$W = \int_{F_{A0}}^{F_A} \frac{dF_A}{r'_A} \quad (1-14)$$

To obtain some insight into things to come, consider the following example of how one can use the tubular reactor design equation (1-10).

Example 1-3 How Large Is It?

The first-order reaction



is carried out in a tubular reactor in which the volumetric flow rate, v , is constant. Derive an equation relating the reactor volume to the entering and exiting concentrations of A , the rate constant k , and the volumetric flow rate v . Determine the reactor volume necessary to reduce the exiting concentration to 10% of the entering concentration when the volumetric flow rate is 10 dm³/min (i.e., liters/min) and the specific reaction rate, k , is 0.23 min⁻¹.

Solution

For a tubular reactor, the mole balance on species A ($j = A$) was shown to be

$$\frac{dF_A}{dV} = r_A \quad (1-10)$$

For a first-order reaction, the rate law (discussed in Chapter 3) is

$$-r_A = kC_A \quad (\text{E1-3.1})$$

Since the volumetric flow rate, v_0 , is constant,

$$\frac{dF_A}{dV} = \frac{d(C_A v_0)}{dV} = v_0 \frac{dC_A}{dV} = r_A \quad (\text{E1-3.2})$$

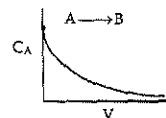
Substituting for r_A in Equation (E1-3.1) yields

$$-\frac{v_0 dC_A}{dV} = -r_A = kC_A \quad (\text{E1-3.3})$$

Use differential form of design equation for catalyst decay and pressure drop



Reactor sizing



Rearranging gives

$$-\frac{v_0}{k} \left(\frac{dC_A}{C_A} \right) = dV$$

Using the conditions at the entrance of the reactor that when $V = 0$, then $C_A = C_{A0}$,

$$-\frac{v_0}{k} \int_{C_{A0}}^{C_A} \frac{dC_A}{C_A} = \int_0^V dV \quad (\text{E1-3.4})$$

This equation gives

$$V = \frac{v_0}{k} \ln \frac{C_{A0}}{C_A} \quad (\text{E1-3.5})$$

Substituting C_{A0} , C_A , v_0 , and k in Equation (E1-3.5), we have

$$V = \frac{10 \text{ dm}^3/\text{min}}{0.23 \text{ min}^{-1}} \ln \frac{C_{A0}}{0.1 C_{A0}} = \frac{10 \text{ dm}^3}{0.23} \ln 10 = 100 \text{ dm}^3 \text{ (i.e., 100 L; 0.1 m}^3\text{)}$$

We see that a reactor volume of 0.1 m^3 is necessary to convert 90% of species A entering into product B.

In the remainder of this chapter we look at slightly more detailed drawings of some typical industrial reactors and point out a few of the advantages and disadvantages of each.²

1.5 Industrial Reactors

A batch reactor is used for small-scale operation, for testing new processes that have not been fully developed, for the manufacture of expensive products, and for processes that are difficult to convert to continuous operations. The reactor can be charged (i.e., filled) through the holes at the top (Figure 1-8). The batch reactor has the advantage of high conversions that can be obtained by leaving the reactant in the reactor for long periods of time, but it also has the disadvantages of high labor costs per batch and the difficulty of large-scale production.

Liquid-Phase Reactions. Although a semibatch reactor (Figure 1-9) has essentially the same disadvantages as the batch reactor, it has the advantages of good temperature control and the capability of minimizing unwanted side reactions through the maintenance of a low concentration of one of the reactants. The semibatch reactor is also used for two-phase reactions in which a gas is usually bubbled continuously through the liquid.

A continuous-stirred tank reactor (CSTR) is used when intense agitation is required. A photo showing a cutaway view of a Pfaudler CSTR/batch reactor is presented in Figure 1-10. Table 1-1 gives the typical sizes (along with that of

² *Chem. Eng.*, 63(10), 211 (1956). See also *AIChE Modular Instruction Series E*, Vol. 5 (1984).

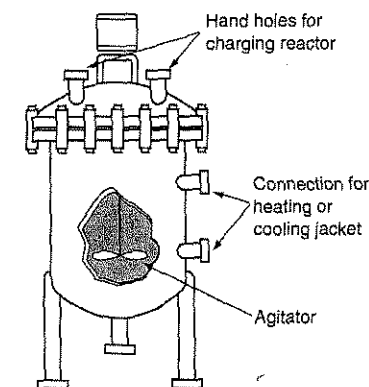


Figure 1-8 Simple batch homogeneous reactor. [Excerpted by special permission from *Chem. Eng.*, 63(10), 211 (Oct. 1956). Copyright 1956 by McGraw-Hill, Inc., New York, NY 10020.]

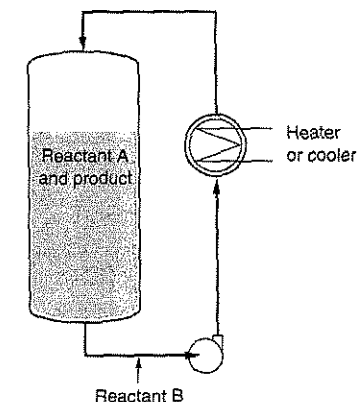


Figure 1-9 Semibatch reactor. [Excerpted by special permission from *Chem. Eng.*, 63(10), 211 (Oct. 1956). Copyright 1956 by McGraw-Hill, Inc., New York, NY 10020.]

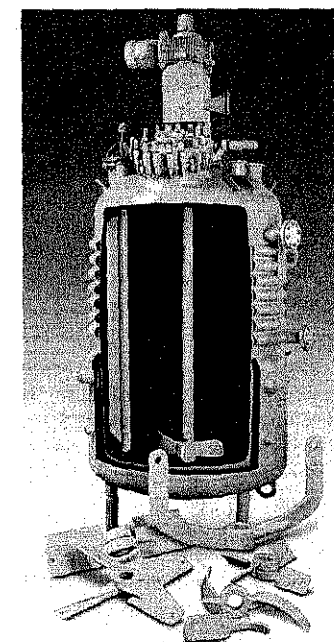


Figure 1-10 CSTR/batch reactor. (Courtesy of Pfaudler, Inc.)

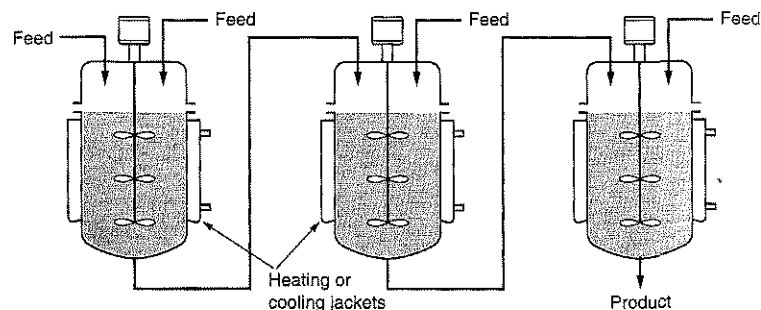
When is a batch reactor used?

What are the advantages and disadvantages of a CSTR?



TABLE 1-1. REPRESENTATIVE PFAUDLER CSTR/BATCH REACTOR SIZES AND 1996 PRICES

Volume	Price	Volume	Price
5 Gallons (wastebasket)	\$27,000	1000 Gallons (2 Jacuzzis)	\$80,000
50 Gallons (garbage can)	\$35,000	4000 Gallons (8 Jacuzzis)	\$143,000
500 Gallons (Jacuzzi)	\$67,000	8000 Gallons (gasoline tanker)	\$253,000

Figure 1-11 Battery of stirred tanks. [Excerpted by special permission from *Chem. Eng.*, 63(10), 211 (Oct. 1956). Copyright 1956 by McGraw-Hill, Inc., New York, NY 10020.]

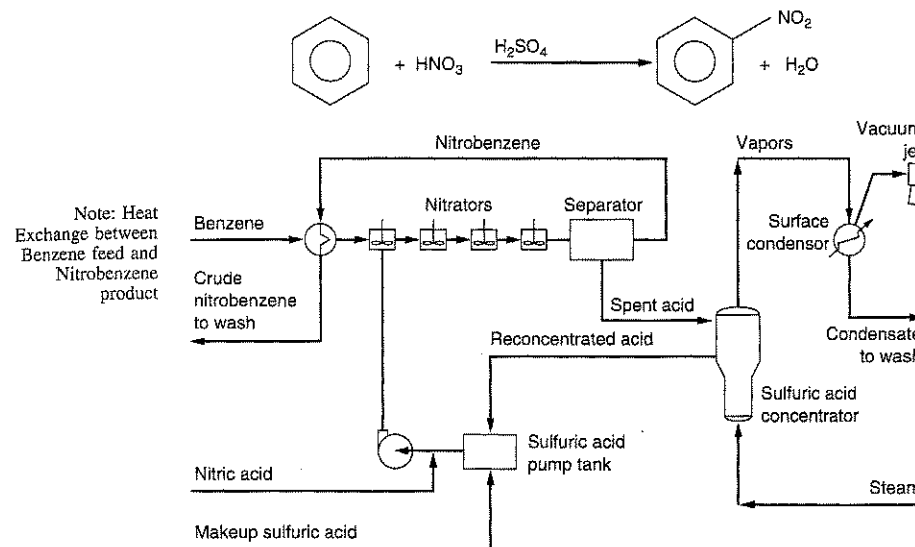
the comparable size of a familiar object) and costs for batch and CSTR reactors. All reactors are glass lined and the prices include heating/cooling jacket, motor, mixer, and baffles. The reactors can be operated at temperatures between 20 and 450°F and at pressures up to 100 psi.

The CSTR can either be used by itself or, in the manner shown in Figure 1-11, as part of a series or battery of CSTRs. It is relatively easy to maintain good temperature control with a CSTR. There is, however, the disadvantage that the conversion of reactant per volume of reactor is the smallest of the flow reactors. Consequently, very large reactors are necessary to obtain high conversions.

If you are not able to afford to purchase a new reactor, it may be possible to find a used reactor that may fit your needs. Previously owned reactors are much less expensive and can be purchased from equipment clearinghouses such as Universal Process Equipment or Loeb Equipment Supply.

Example 1-4 Liquid-Phase Industrial Process Flowsheet

A battery of four CSTRs similar to those in Figure 1-10 are shown in the plant flow-sheet (Figure E1-4.1) for the commercial production of nitrobenzene. In 1995, 1.65 billion pounds of nitrobenzene were produced.

Figure E1-4.1 Flowsheet for the production of nitrobenzene. [Adapted from *Process Technology and Flowsheet*, Vol. II, reprints from *Chemical Engineering* (New York: McGraw-Hill, 1983), p. 125.]

In 1980 the operating requirements (per ton of nitrobenzene) were as follows (utilities and feedstock requirements have been minimized by recycling sulfuric acid):

Raw materials	
Benzene	0.64 ton
Nitric acid (100%)	0.515 ton
Sulfuric acid (100%)	0.0033 ton
Caustic soda	0.004 ton
Utilities	
Cooling water	14,200 gal
Steam	800 lb
Electricity	20 kWh
Compressed air	180 Scf/m

The feed consists of 3 to 7% HNO_3 , 59 to 67% H_2SO_4 , and 28 to 37% water. Sulfuric acid is necessary to adsorb the water and energy generated by the heat of reaction. The plant, which produces 15,000 lb nitrobenzene/h, requires one or two operators per shift together with a plant supervisor and part-time foreman. This exothermic reaction is carried out essentially adiabatically, so that the temperature of the feed stream rises from 90°C to 135°C at the exit. One observes that the nitrobenzene stream from the separator is used to heat the benzene feed. However, care must be taken so that the temperature never exceeds 190°C, where secondary reactions could result in an explosion. One of the safety precautions is the installation of relief valves that will rupture before the temperature approaches 190°C, thereby allowing a boil-off of water and benzene, which would drop the reactor temperature.

What are the advantages and disadvantages of a PFR?

CSTR: liquids
PFR: gases

Gas-Phase Reactions. The tubular reactor [i.e., plug-flow reactor (PFR)] is relatively easy to maintain (no moving parts), and it usually produces the highest conversion per reactor volume of any of the flow reactors. The disadvantage of the tubular reactor is that it is difficult to control temperature within the reactor, and hot spots can occur when the reaction is exothermic. The tubular reactor is commonly found either in the form of one long tube or as one of a number of shorter reactors arranged in a tube bank as shown in Figure 1-12. Most homogeneous liquid-phase flow reactors are CSTRs, whereas most homogeneous gas-phase flow reactors are tubular.

The costs of PFR and PBR (without catalyst) are similar to the costs of heat exchangers and thus can be found in *Plant Design and Economics for*

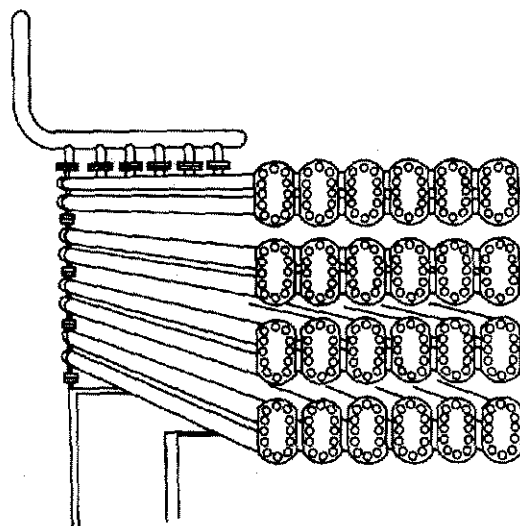


Figure 1-12 Longitudinal tubular reactor. [Excerpted by special permission from *Chem. Eng.*, 63(10), 211 (Oct. 1956). Copyright 1956 by McGraw-Hill, Inc., New York, NY 10020.]

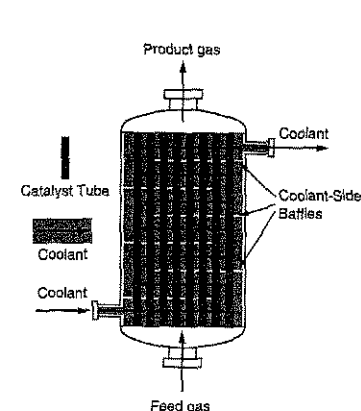


Figure 1-13 Longitudinal catalytic packed-bed reactor. [From Cropley, *American Institute of Chemical Engineers*, 86(2), 34 (1990). Reproduced with permission of the American Institute of Chemical Engineers, Copyright © 1990 AIChE. All rights reserved.]

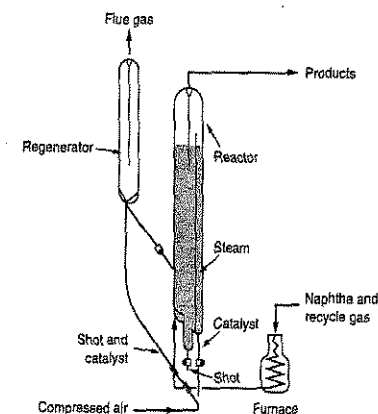


Figure 1-14 Fluidized-bed catalytic reactor. [Excerpted by special permission from *Chem. Eng.*, 63(10), 211 (Oct. 1956). Copyright 1956 by McGraw-Hill, Inc., New York, NY 10020.]

Chemical Engineers, 4th ed., by M. S. Peters and K. D. Timmerhaus (New York: McGraw-Hill, 1991). From Figure 15-12 of this book, one can get an estimate of the purchase cost per foot of \$1 for a 1-in. pipe and \$2 per foot for a 2-in. pipe for single tubes and approximately \$20 to \$50 per square foot of surface area for fixed-tube sheet exchangers.

A packed-bed (also called a fixed-bed) reactor is essentially a tubular reactor that is packed with solid catalyst particles (Figure 1-13). This heterogeneous reaction system is used most frequently to catalyze gas reactions. This reactor has the same difficulties with temperature control as other tubular reactors, and in addition, the catalyst is usually troublesome to replace. On occasion, channeling of the gas flow occurs, resulting in ineffective use of parts of the reactor bed. The advantage of the packed-bed reactor is that for most reactions it gives the highest conversion per weight of catalyst of any catalytic reactor.

Another type of catalytic reactor in common use is the fluidized-bed (Figure 1-14). The fluidized-bed reactor is analogous to the CSTR in that its contents, though heterogeneous, are well mixed, resulting in an even temperature distribution throughout the bed. The fluidized-bed reactor cannot be modeled as either a CSTR or a tubular reactor (PFR), but requires a model of its own. The temperature is relatively uniform throughout, thus avoiding hot spots. This type of reactor can handle large amounts of feed and solids and has good temperature control; consequently, it is used in a large number of applications. The advantages of the ease of catalyst replacement or regeneration are

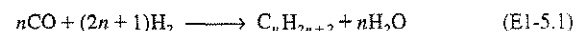
sometimes offset by the high cost of the reactor and catalyst regeneration equipment.

Example 1-5 Gas-Phase Industrial Reactor/Process

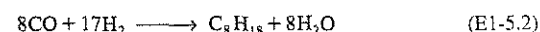
Synthesis gas contains a mixture of carbon monoxide and hydrogen and can be obtained from the combustion of coal or natural gas. This gas can be used to produce synthetic crude by the Fischer-Tropsch reaction. Describe two industrial reactors used to convert synthesis gas to a mixture of hydrocarbons by the Fischer-Tropsch process.

Solution

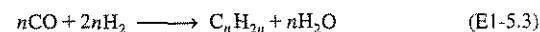
Reactions. The Fischer-Tropsch reaction converts synthesis gas into a mixture of alkanes and alkenes over a solid catalyst usually containing iron. The basic reaction for paraffin formation is as follows



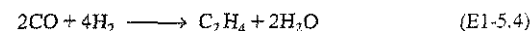
For example, when octane, a component of gasoline, is formed, Equation (E1-5.1) becomes



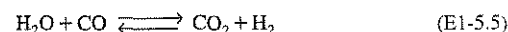
Similarly, for the formation of olefins,



For ethylene formation, Equation (E1-5.3) becomes



The other type of main reaction that occurs in this process is the water-gas-shift reaction



In addition to the simultaneous formation of paraffins and olefins, side reactions also take place to produce small quantities of acids and nonacids (e.g., ethanol).

Reactors. Two types of reactors will be discussed, a *straight-through transport reactor*, which is also referred to as a *riser* or *circulating fluidized bed*, and a *packed-bed reactor* (PBR), which is also referred to as a *fixed-bed reactor*.

Riser. Because the catalyst used in the process decays rapidly at high temperatures (e.g., 350°C), a *straight-through transport reactor* (STTR) (Chapter 10) is used. This type of reactor is also called a *riser* and/or a *circulating bed*. A schematic diagram is shown in Figure E1-5.1. Here the catalyst particles are fed to the bottom of the reactor and are shot up through the reactor together with the entering reactant gas mixture and then separated from the gas in a settling hopper. The volumetric gas feed rate of $3 \times 10^5 \text{ m}^3/\text{h}$ is roughly equivalent to feeding the volume of gas contained in the University of Michigan football stadium to the reactor each hour.

A schematic and photo of an industrial *straight-through transport reactor* used at Sasol are shown in Figure E1-5.2 together with the composition of the feed and product streams. The products that are condensed out of the product stream

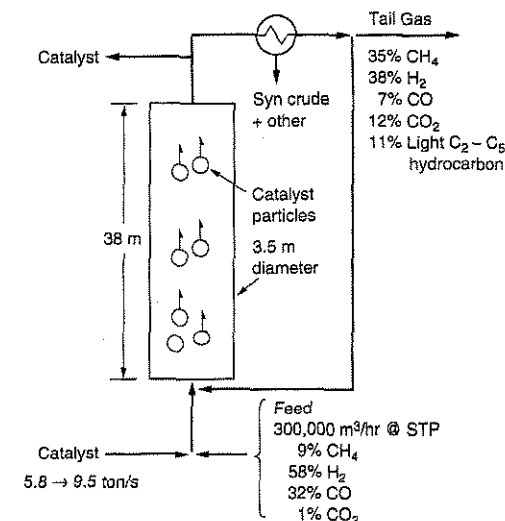


Figure E1-5.1 Schematic of Sasol Fischer-Tropsch process.

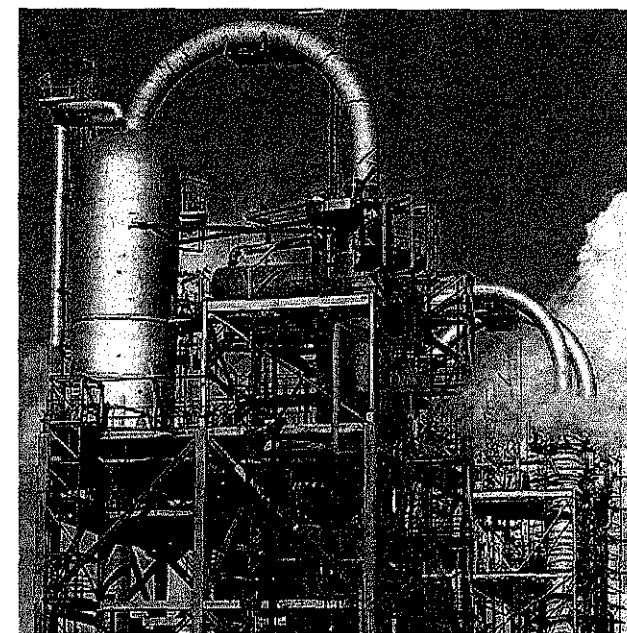
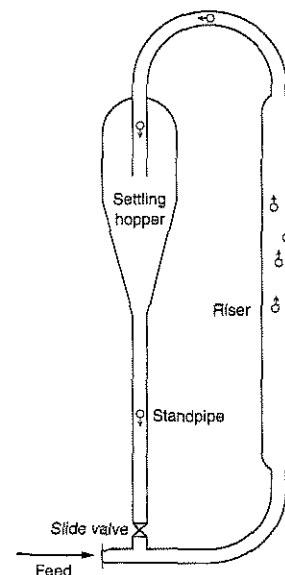


Figure E1-5.2 The reactor is 3.5 m in diameter and 38 m tall. (Schematic and photo courtesy of Sasol/Sastech PT Limited.)

before the stream is recycled include Synoil (a synthetic crude), water, methyl ethyl ketone (MEK), alcohols, acids, and aldehydes. The reactor is operated at 25 atm and 350°C and at any one time contains 150 tons of catalyst. The catalyst feed rate is 6 to 9.5 tons/s, and the gas recycle ratio is 2:1.

Packed Bed. The packed-bed reactor used at the Sasol plant to carry out Fischer-Tropsch synthesis reaction is shown in Figure E1-5.3. Synthesis gas is fed at a rate of 30,000 m³/h (STP) at 240°C and 27 atm to the packed-bed reactor. The reactor contains 2050 tubes, each of which is 5.0 cm in diameter and 12 m in length. The iron-based catalyst that fills these tubes usually contains K₂O and SiO₂ and has a specific area on the order of 200 m²/g. The reaction products are light hydrocarbons along with a wax that is used in candles and printing inks. Approximately 50% conversion of the reactant is achieved in the reactor.

Use to produce wax
for candles and
printing inks.

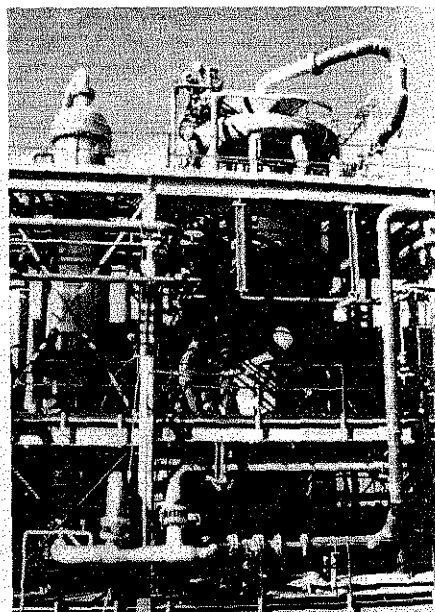
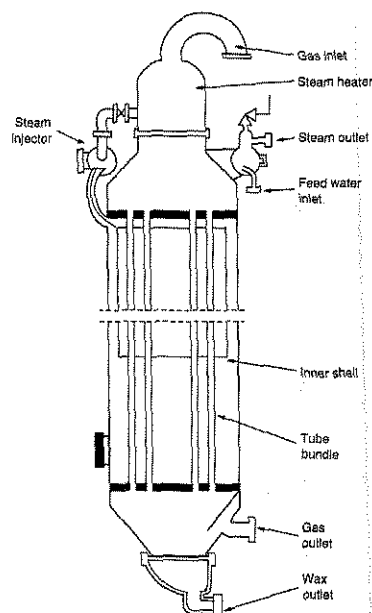


Figure E1-5.3 Packed-bed reactor. (Schematic and photograph courtesy of Sasol/Sastech PT Limited.)

The aim of the preceding discussion on commercial reactors is to give a more detailed picture of each of the major types of industrial reactors: batch, semibatch, CSTR, tubular, fixed-bed (packed-bed), and fluidized-bed. Many variations and modifications of these commercial reactors are in current use; for further elaboration, refer to the detailed discussion of industrial reactors given by Walas.³

³ S. M. Walas, *Reaction Kinetics for Chemical Engineers* (New York: McGraw-Hill, 1959), Chap. 11.

SUMMARY

1. A mole balance on species j , which enters, leaves, reacts, and accumulates in a system volume V , is

$$F_{j0} - F_j + \int_V r_j dV = \frac{dN_j}{dt} \quad (\text{S1-1})$$

2. The kinetic rate law for r_j is:

- Solely a function of properties of reacting materials [e.g., concentration (activities), temperature, pressure, catalyst or solvent (if any)].
- An intensive quantity.
- An algebraic equation, not a differential equation.

For homogeneous catalytic systems, typical units of $-r_j$ may be gram moles per second per liter; for heterogeneous systems, typical units of r_j' may be gram moles per second per gram of catalyst. By convention, $-r_A$ is the rate of disappearance of species A and r_A is the rate of formation of species A.

3. Mole balances on four common reactors are as follows:

Reactor	Mole Balance	Comment
Batch	$\frac{dN_j}{dt} = r_j V$	No spatial variation
CSTR	$V = \frac{F_{j0} - F_j}{-r_j}$	No spatial variation, steady state
PFR	$\frac{dF_j}{dV} = r_j$	Steady state
PBR	$\frac{dF_j}{dW} = r_j'$	Steady state

QUESTIONS AND PROBLEMS

I wish I had an answer for that, because I'm getting tired of answering that question.

Yogi Berra, New York Yankees
Sports Illustrated, June 11, 1984

The subscript to each of the problem numbers indicates the level of difficulty: A, least difficult; D, most difficult.

A = ● B = ■ C = ♦ D = ♦♦

In each of the questions and problems below, rather than just drawing a box around your answer, write a sentence or two describing how you solved the problem, the assumptions you made, the reasonableness of your answer, what you learned, and any other facts that you want to include. You may wish to refer to W. Strunk and E. B. White, *The Elements of Style* (New York: Macmillan, 1979) and Joseph M. Williams, *Style: Ten Lessons in Clarity & Grace* (Glenview, Ill.: Scott, Foresman, 1989) to enhance the quality of your sentences.



P1-1_A After reading each page, ask yourself a question. Make a list of the most important things that you learned in this chapter.

P1-2_A What if:

- the benzene feed stream in Example 1-4 were not preheated by the product stream? What would be the consequences?
- you needed the cost of a 6000-gallon and a 15,000-gallon Pfaudler reactor? What would they be?
- the exit concentration of A in Example 1-3 were specified at 0.1% of the entering concentration?
- the volume of the movable piston in Example 1-2 varied in a manner similar to a car cylinder, $V = V_0 + V_1 \sin \omega t$?
- only one operator showed up to run the nitrobenzene plant, what would be some of your first concerns?

P1-3_B Calculate the volume of a CSTR for the conditions used to calculate the plug-flow reactor volume in Example 1-3.

P1-4_A Calculate the time to reduce the number of moles of A to 1% of its initial value in a constant-volume batch reactor for the reaction and data in Example 1-3.

P1-5_A What assumptions were made in the derivation of the design equation for:

- the batch reactor?
 - the CSTR?
 - the plug-flow reactor (PFR)?
 - the packed-bed reactor (PBR)?
- (e) State in words the meanings of $-r_A$, $-r'_A$, and r'_A . Is the reaction rate $-r_A$ an extensive quantity? Explain.

P1-6_A What is the difference between the rate of reaction for a homogeneous system, $-r_A$, and the rate of reaction for a heterogeneous system, $-r'_A$? Use the mole balance to derive an equation analogous to Equation (1-6) for a fluidized CSTR containing catalyst particles in terms of the catalyst weight, W , and other appropriate terms.

P1-7_A How can you convert the general mole balance equation for a given species, Equation (1-4), to a general mass balance equation for that species?

P1-8_A The United States produces 24% of the world's chemical products. According to the yearly "Facts and Figures" issue of *Chemical and Engineering News* (*C&E News*, June 24, 1996), the following were the 10 most produced chemicals in 1995:

Chemical	Billions of Pounds	Chemical	Billions of Pounds
1. H ₂ SO ₄	95.36	6. NH ₃	35.60
2. N ₂	68.04	7. H ₃ PO ₄	26.19
3. O ₂	53.48	8. NaOH	26.19
4. C ₂ H ₄	46.97	9. C ₃ H ₆	25.69
5. CaO	41.23	10. Cl ₂	25.09

- (a) What were the 10 most produced chemicals for the year that just ended? Were there any significant changes from the 1995 statistics? The same issue of *C&E News* gives the following chemical companies as the top 10 in total sales in 1995. (Also see <http://www.chemweek.com>)



Company	Sales (billions of dollars)
1. Dow	19.73
2. Dupont	18.43
3. Exxon	11.73
4. Hoechst Celanese	7.39
5. Monsanto	7.25
6. General Electric	6.63
7. Mobil	6.15
8. Union Carbide	5.89
9. Amoco	5.66
10. Occidental Petroleum	5.41

- What 10 companies were tops in sales for the year just ended? Did any significant changes occur compared to the 1995 statistics?
- Why do you think H₂SO₄ is the most produced chemical? What are some of its uses?
- What is the current annual production rate (lb/yr) of ethylene, ethylene oxide, and benzene?
- Why do you suspect there are so few organic chemicals in the top 10?

P1-9_A Referring to the text material and the additional references on commercial reactors given at the end of this chapter, fill in the following table:

Type of Reactor	Characteristics	Kinds of Phases Present	Use	Advantages	Disadvantages
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____

P1-10_B Schematic diagrams of the Los Angeles basin are shown in Figure P1-10. The basin floor covers approximately 700 square miles (2×10^{10} ft²) and is almost completely surrounded by mountain ranges. If one assumes an inversion height in the basin of 2000 ft, the corresponding volume of air in the basin is 4×10^{13} ft³. We shall use this system volume to model the accumulation and depletion of air pollutants. As a very rough first approximation, we shall treat the Los Angeles basin as a well-mixed container (analogous to a CSTR) in which there are no spatial variations in pollutant concentrations. Consider only the pollutant carbon monoxide and assume that the source of CO is from automobile exhaust and that, on the average, there are 400,000 cars operating in the basin at any one time. Each car gives off roughly 3000 standard cubic feet of exhaust each hour containing 2 mol % carbon monoxide.

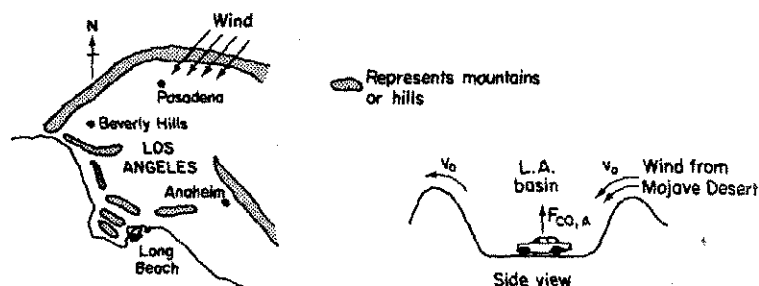


Figure P1-10

We shall perform an unsteady-state mole balance on CO as it is depleted from the basin area by a Santa Ana wind. Santa Ana winds are high-velocity winds that originate in the Mojave Desert just to the northeast of Los Angeles. This clean desert air flows into the basin through a corridor assumed to be 20 miles wide and 2000 ft high (inversion height) replacing the polluted air, which flows out to sea or toward the south. The concentration of CO in the Santa Ana wind entering the basin is 0.08 ppm (2.04×10^{-10} lb mol/ft³).

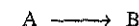
- How many pound moles of gas are in the system volume we have chosen for the Los Angeles basin if the temperature is 75°F and the pressure is 1 atm? (Values of the ideal gas constant may be found in Appendix B.)
- What is the rate, $F_{CO,A}$, at which all autos emit carbon monoxide into the basin (lb mol CO/h)?
- What is the volumetric flow rate (ft³/h) of a 15-mph wind through the corridor 20 miles wide and 2000 ft high? (Ans.: 1.67×10^{13} ft³/h.)
- At what rate, $F_{CO,S}$, does the Santa Ana wind bring carbon monoxide into the basin (lb mol/h)?
- Assuming that the volumetric flow rates entering and leaving the basin are identical, $v = v_0$, show that the unsteady mole balance on CO within the basin becomes

$$F_{CO,A} + F_{CO,S} - v_0 C_{CO} = V \frac{dC_{CO}}{dt} \quad (P1-10.1)$$

- Verify that the solution to Equation (P1-10.1) is

$$t = \frac{V}{v_0} \ln \frac{F_{CO,A} + F_{CO,S} - v_0 C_{CO,0}}{F_{CO,A} + F_{CO,S} - v_0 C_{CO}} \quad (P1-10.2)$$

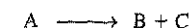
- If the initial concentration of carbon monoxide in the basin before the Santa Ana wind starts to blow is 8 ppm (2.04×10^{-8} lb mol/ft³), calculate the time required for the carbon monoxide to reach a level of 2 ppm.
- Repeat parts (b) through (g) for another pollutant, NO. The concentration of NO in the auto exhaust is 1500 ppm (3.84×10^{-6} lb mol/ft³), and the initial NO concentration in the basin is 0.5 ppm. If there is no NO in the Santa Ana wind, calculate the time for the NO concentration to reach 0.1 ppm. What is the lowest concentration of NO that could be reached?

P1-11_A The reaction

is to be carried out isothermally in a continuous-flow reactor. Calculate both the CSTR and PFR reactor volumes necessary to consume 99% of A (i.e., $C_A = 0.01C_{A0}$) when the entering molar flow rate is 5 mol/h, assuming the reaction rate $-r_A$ is:

- $-r_A = k$ with $k = 0.05 \frac{\text{mol}}{\text{h} \cdot \text{dm}^3}$ (Ans.: $V = 99 \text{ dm}^3$)
- $-r_A = kC_A$ with $k = 0.0001 \text{ s}^{-1}$
- $-r_A = kC_A^2$ with $k = 3 \frac{\text{dm}^3}{\text{mol} \cdot \text{h}}$ (Ans.: $V_{\text{CSTR}} = 66,000 \text{ dm}^3$)

The entering volumetric flow rate is 10 dm³/h. [Note: $F_A = C_A v$. For a constant volumetric flow rate $v = v_0$, then $F_A = C_A v_0$. Also, $C_{A0} = F_{A0}/v_0 = (5 \text{ mol/h})/(10 \text{ dm}^3/\text{h}) = 0.5 \text{ mol/dm}^3$.]

P1-12_C The gas-phase reaction

is carried out isothermally in a 20-dm³ constant-volume batch reactor. Twenty moles of pure A is initially placed in the reactor. The reactor is well mixed.

- If the reaction is first order:

$$-r_A = kC_A \quad \text{with } k = 0.865 \text{ min}^{-1}$$

calculate the time necessary to reduce the number of moles of A in the reactor to 0.2 mol. (Note: $N_A = C_A V$) (Ans.: $t = 5.3 \text{ min}$)

- If the reaction is second order:

$$-r_A = kC_A^2 \quad \text{with } k = \frac{2 \text{ dm}^3}{\text{mol} \cdot \text{min}}$$

calculate the time necessary to consume 19.0 mol of A.

- If the temperature is 127°C, what is the initial total pressure? What is the final total pressure assuming the reaction goes to completion?

P1-13_A

- How many cubic feet (at STP) enter the packed-bed reactor described in Example 1-5 every second? How long does a molecule spend, on the average, in the reactor? [Hint: What is the gas velocity in each tube assuming a 30% porosity (volume of gas/volume of reactor) for the packed bed?]

- Estimate the time that a catalyst particle and a gas-phase molecule spend in the Sasol straight-through transport reactor (STTR). What is the bulk density of the catalyst (kg cat/m³) in the STTR?

P1-14_A

Write a one-paragraph summary of a journal article on chemical kinetics or reaction engineering. The article must have been published within the last five years.⁴ What did you learn from this article? Why is the article important?

- What journals, books, or papers give you costs of industrial (not laboratory, e.g., Fisher catalog) chemicals and catalysts?
- List various journals, books, or other sources where you will find details about the construction and safety of industrial reactors.

⁴ See the Supplementary Reading list at the end of the chapter, particularly item 4.

- P1-16_C** What are typical operating conditions (temperature, pressure) of a catalytic cracking reactor used in petroleum refining?
- P1-17_A** View the photos and schematics on the CD-ROM under Elements of Chemical Reaction Engineering—Chapter 1. Look at the quicktime videos. Write a paragraph describing two or more of the reactors. What similarities and differences do you observe between the reactors on the Web and in the text?
- P1-18_A** (a) There are initially 500 rabbits (x) and 200 foxes (y) on Farmer Oat's property. Use POLYMATH or MATLAB to plot the concentration of foxes and rabbits as a function of time for a period of up to 500 days. The predator-prey relationships are given by the following set of coupled ordinary differential equations:

$$\frac{dx}{dt} = k_1 x - k_2 x \cdot y$$

$$\frac{dy}{dt} = k_3 x \cdot y - k_4 y$$

Constant for growth of rabbits $k_1 = 0.02 \text{ day}^{-1}$

Constant for death of rabbits $k_2 = 0.00004/(\text{day} \times \text{no. of foxes})$

Constant for growth of foxes after eating rabbits $k_3 = 0.0004/(\text{day} \times \text{no. of rabbits})$

Constant for death of foxes $k_4 = 0.04 \text{ day}^{-1}$

What do your results look like for the case of $k_3 = 0.00004/(\text{day} \times \text{no. of rabbits})$ and $t_{\text{final}} = 800$ days? Also plot the number of foxes versus the number of rabbits. Explain why the curves look the way they do.

Vary the parameters k_1 , k_2 , k_3 , and k_4 . Discuss which parameters can or cannot be larger than others. Write a paragraph describing what you find.

- (b) Use POLYMATH or MATLAB to solve the following set of nonlinear algebraic equations:

$$x^3 y - 4y^2 + 3x = 1$$

$$6y^2 - 9xy = 5$$

with initial guesses of $x = 2$, $y = 2$. Try to become familiar with the edit keys in POLYMATH MatLab. See CD-ROM for instructions.

- P1-19_A** (a) Surf the World Wide Web and make a list of the links that are relevant to chemical reaction engineering. Pick the five most relevant links and write two or three sentences about each.
- (b) Check the reaction engineering 3rd ed. web site (<http://www.engin.umich.edu/~cre>) to learn what material has been added and any typographical errors that have been found in the first printing.
- P1-20_A** Surf the CD-ROM included with the text.
- (a) Approximately how many additional solved example problems are there?
- (b) List at least one video clip.
- (c) In what lectures are activation energy discussed?
- (d) What photos are in the Wetlands Module?

After Reading Each Page in
This Book, Ask Yourself a Question
About What You Read

CD-ROM MATERIAL

• Learning Resources

1. *Summary Notes for Lectures 1 and 2*

2. *Web Modules*

A. Problem Solving Algorithm for Closed-Ended Problems

B. Hints for Getting Unstuck on a Problem

3. *Interactive Computer Modules*

A. Quiz Show I

4. *Solved Problems*

A. CDP1-A_B Batch Reactor Calculations: A Hint of Things to Come

• Professional Reference Shelf

1. *Photographs of Real Reactors*

• **FAQ [Frequently Asked Questions]**— In Updates/FAQ icon section

• **Additional Homework Problems**

CDP1-A_A Calculate the time to consume 80% of species A in a constant-volume batch reactor for a first- and a second-order reaction. (Includes Solution)

CDP1-B_A Derive the differential mole balance equation for a foam reactor. [2nd Ed. P1-10_B]

SUPPLEMENTARY READING

- For further elaboration of the development of the general balance equation, see
DIXON, D. C., *Chem. Eng. Sci.*, 25, 337 (1970).
FELDER, R. M., and R. W. ROUSSEAU, *Elementary Principles of Chemical Processes*, 2nd ed. New York: Wiley, 1986, Chap. 4.
HIMMELBLAU, D. M., *Basic Principles and Calculations in Chemical Engineering*, 6th ed. Upper Saddle River, N.J.: Prentice Hall, 1996, Chaps. 2 and 6.
HOLLAND, C. D., and R. G. ANTHONY, *Fundamentals of Chemical Reaction Engineering*, 2nd ed. Upper Saddle River, N.J.: Prentice Hall, 1989, Chap. 1.
 - A detailed explanation of a number of topics in this chapter can be found in
CRYNES, B. L., and H. S. FOGLER, eds., *AIChE Modular Instruction Series E: Kinetics*, Vols. 1 and 2. New York: AIChE, 1981.
 - An excellent description of the various types of commercial reactors used in industry is found in Chapter 11 of
WALAS, S. M., *Reaction Kinetics for Chemical Engineers*. New York: McGraw-Hill, 1959.
- A somewhat different discussion of the usage, advantages, and limitations of various reactor types can be found in
DENBIGH, K. G., and J. C. R. TURNER, *Chemical Reactor Theory*, 2nd ed. Cambridge: Cambridge University Press, 1971, pp. 1–10.

4. A discussion of some of the most important industrial processes is presented by MEYERS, R.A., *Handbook of Chemical Production Processes*. New York: McGraw-Hill, 1986.
- See also
- MCKETTA, J. J., ed., *Encyclopedia of Chemical Processes and Design*. New York: Marcel Dekker, 1976.
- A similar book, which describes a larger number of processes, is
- SHREVE, R. N., and J. A. BRINK, JR., *Chemical Process Industries*, 4th ed. New York: McGraw-Hill, 1977.
5. The following journals may be useful in obtaining information on chemical reaction engineering: *International Journal of Chemical Kinetics*, *Journal of Catalysis*, *Journal of Applied Catalysis*, *AIChE Journal*, *Chemical Engineering Science*, *Canadian Journal of Chemical Engineering*, *Chemical Engineering Communications*, *Journal of Physical Chemistry*, and *Industrial and Engineering Chemistry Research*.
 6. The price of chemicals can be found in such journals as the *Chemical Marketing Reporter*, *Chemical Weekly*, and *Chemical Engineering News*.

Conversion 2 and Reactor Sizing

Be more concerned with your character than with your reputation, because character is what you really are while reputation is merely what others think you are.
John Wooden, coach, UCLA Bruins

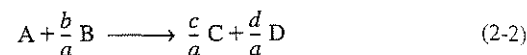
The first chapter focused on the general mole balance equation; the balance was applied to the four most common types of industrial reactors, and a design equation was developed for each reactor type. In Chapter 2 we first define *conversion* and then rewrite the design equations in terms of conversion. After carrying out this operation, we show how one may *size* a reactor (i.e., determine the reactor volume necessary to achieve a specified conversion) once the relationship between reaction rate, r_A , and conversion is known.

2.1 Definition of Conversion

In defining conversion, we choose one of the reactants as the basis of calculation and then relate the other species involved in the reaction to this basis. In most instances it is best to choose the limiting reactant as the basis of calculation. We develop the stoichiometric relationships and design equations by considering the general reaction



The uppercase letters represent chemical species and the lowercase letters represent stoichiometric coefficients. Taking species A as our *basis of calculation*, we divide the reaction expression through by the stoichiometric coefficient of species A, in order to arrange the reaction expression in the form



to put every quantity on a "per mole of A" basis.

Now we ask such questions as "How can we quantify how far a reaction [e.g., Equation (2-2)] has progressed?" or "How many moles of C are formed for every mole A consumed?" A convenient way to answer these questions is to define a parameter called *conversion*. The conversion X_A is the number of moles of A that have reacted per mole of A fed to the system:

Definition of X

$$X_A = \frac{\text{moles of A reacted}}{\text{moles of A fed}}$$

Because we are defining conversion with respect to our basis of calculation [A in Equation (2-2)], we eliminate the subscript A for the sake of brevity and let $X \equiv X_A$.

2.2 Design Equations

2.2.1 Batch Systems

In most batch reactors, the longer a reactant is in the reactor, the more reactant is converted to product until either equilibrium is reached or the reactant is exhausted. Consequently, in batch systems the conversion X is a function of the time the reactants spend in the reactor. If N_{A0} is the number of moles of A initially, then the total number of moles of A that have reacted after a time t is $[N_{A0}X]$

$$\begin{aligned} \left[\begin{array}{c} \text{moles of A} \\ \text{consumed} \end{array} \right] &= \left[\begin{array}{c} \text{moles of A} \\ \text{fed} \end{array} \right] \cdot \left[\begin{array}{c} \text{moles of A reacted} \\ \text{mole of A fed} \end{array} \right] \\ \left[\begin{array}{c} \text{moles of A} \\ \text{reacted} \\ \text{(consumed)} \end{array} \right] &= [N_{A0}] \cdot [X] \end{aligned} \quad (2-3)$$

Now, the number of moles of A that remain in the reactor after a time t , N_A , can be expressed in terms of N_{A0} and X :

$$\begin{aligned} \left[\begin{array}{c} \text{moles of A} \\ \text{in reactor} \\ \text{at time } t \end{array} \right] &= \left[\begin{array}{c} \text{moles of A} \\ \text{initially fed} \\ \text{to reactor at} \\ t = 0 \end{array} \right] - \left[\begin{array}{c} \text{moles of A that} \\ \text{have been con-} \\ \text{sumed by chemical} \\ \text{reaction} \end{array} \right] \\ [N_A] &= [N_{A0}] - [N_{A0}X] \end{aligned}$$

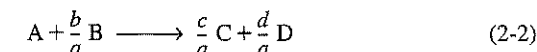
The number of moles of A in the reactor after a conversion X has been achieved is

$$N_A = N_{A0} - N_{A0}X = N_{A0}(1 - X) \quad (2-4)$$

When no spatial variations in reaction rate exist, the mole balance on species A for a batch system reduces to the following equation:

$$\frac{dN_A}{dt} = r_A V \quad (2-5)$$

This equation is valid whether or not the reactor volume is constant. In the general reaction



reactant A is disappearing; therefore, we multiply both sides of Equation (2-5) by -1 to obtain the mole balance for the batch reactor in the form

$$-\frac{dN_A}{dt} = (-r_A)V$$

The rate of disappearance of A, $-r_A$, in this reaction might be given by a rate law similar to Equation (1-2), such as $-r_A = kC_A C_B$.

For batch reactors we are interested in determining how long to leave the reactants in the reactor to achieve a certain conversion X . To determine this length of time, we transform the mole balance, Equation (2-5), in terms of conversion by differentiating Equation (2-4),

$$N_A = N_{A0} - N_{A0}X \quad (2-4)$$

with respect to time, while remembering that N_{A0} is the number of moles of A initially present and is therefore a constant with respect to time.

$$\frac{dN_A}{dt} = 0 - N_{A0} \frac{dX}{dt}$$

Combining the above with Equation (2-5) yields

$$-N_{A0} \frac{dX}{dt} = r_A V$$

For a batch reactor, the design equation in differential form is

Batch reactor
design equation

$$N_{A0} \frac{dX}{dt} = -r_A V \quad (2-6)$$

The differential forms of the design equations often appear in reactor analysis and are particularly useful in the interpretation of reaction rate data.

Constant-volume batch reactors are found very frequently in industry. In particular, the laboratory bomb reactor for gas-phase reactions is widely used for obtaining reaction rate information on a small scale. Liquid-phase reactions in which the volume change during reaction is insignificant are frequently carried out in batch reactors when small-scale production is desired or operating difficulties rule out the use of continuous systems. For a *constant-volume batch reactor*, Equation (2-5) can be arranged into the form

$$-\frac{1}{V} \frac{dN_A}{dt} = -\frac{d(N_A/V)}{dt} = -\frac{dC_A}{dt} = -r_A \quad (2-7)$$

For batch-reactor systems in which the volume varies while the reaction is proceeding, the volume may usually be expressed either as a function of time alone or of conversion alone, for either adiabatic or isothermal reactors. Consequently, the variables of the differential equation (2-6) can be separated in one of the following ways:

$$V dt = N_{A0} \frac{dX}{-r_A}$$

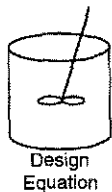
or

$$dt = N_{A0} \frac{dX}{-r_A V}$$

These equations are integrated with the limits that the reaction begins at time zero (i.e., $t = 0$, $X = 0$). When the volume is varied by some external source in a specific manner (such as a car cylinder piston compressing the reacting gas according to the equation $V = V_1 + V_2 \sin \omega t$), the equation relating time and conversion that one would use is

$$\int_0^t V dt = N_{A0} \int_0^X \frac{dX}{-r_A} \quad (2-8)$$

However, for the more common batch reactors in which volume is not a predetermined function of time, the time t necessary to achieve a conversion X is



$$t = N_{A0} \int_0^{X(t)} \frac{dX}{-r_A V} \quad (2-9)$$

Equation (2-6) is the differential form of the design equation, and Equations (2-8) and (2-9) are the integral forms for a batch reactor. The differential form is generally used in the interpretation of laboratory rate data.

2.2.2 Flow Systems

Normally, conversion increases with the time the reactants spend in the reactor. For continuous-flow systems, this time usually increases with increasing reactor volume; consequently, the conversion X is a function of reactor volume V . If F_{A0} is the molar flow rate of species A fed to a system operated at steady state, the molar rate at which species A is reacting within the entire system will be $F_{A0}X$.

$$[F_{A0}] \cdot [X] = \frac{\text{moles of A fed}}{\text{time}} \cdot \frac{\text{moles of A reacted}}{\text{mole of A fed}}$$

$$[F_{A0} \cdot X] = \frac{\text{moles of A reacted}}{\text{time}}$$

The molar feed rate of A to the system *minus* the rate of reaction of A within the system *equals* the molar flow rate of A leaving the system F_A . The preceding sentence can be written in the form of the following mathematical statement:

$$\left[\begin{array}{c} \text{molar flow rate} \\ \text{at which A is} \\ \text{fed to the system} \end{array} \right] - \left[\begin{array}{c} \text{molar rate at} \\ \text{which A is} \\ \text{consumed within} \\ \text{the system} \end{array} \right] = \left[\begin{array}{c} \text{molar flow rate} \\ \text{at which A leaves} \\ \text{the system} \end{array} \right]$$

$$[F_{A0}] - [F_{A0}X] = [F_A]$$

Rearranging gives

$$F_A = F_{A0}(1 - X) \quad (2-10)$$

The entering molar flow rate, F_{A0} (mol/s), is just the product of the entering concentration, C_{A0} (mol/dm³), and the entering volumetric flow rate, v_0 (dm³/s):

$$F_{A0} = C_{A0}v_0$$

For liquid systems, C_{A0} is commonly given in terms of molarity, for example, $C_{A0} = 2$ mol/dm³. For gas systems, C_{A0} can be calculated from the entering temperature and pressure using the ideal gas law or some other gas law. For an ideal gas (see Appendix B):

$$C_{A0} = \frac{P_{A0}}{RT_0} = \frac{y_{A0}P_0}{RT_0}$$

where C_{A0} = entering concentration, mol/dm³

y_{A0} = entering mole fraction of A

P_0 = entering total pressure, kPa

T_0 = entering temperature, K

P_{A0} = entering partial pressure, kPa

R = ideal gas constant (e.g., $R = 8.314 \frac{\text{kPa} \cdot \text{dm}^3}{\text{mol} \cdot \text{K}}$; see Appendix B)

Example 2-1 Using the Ideal Gas Law to Calculate C_{A0}

A gas mixture consists of 50% A and 50% inerts at 10 atm (1013 kPa) and enters the reactor with a flow rate of 6 dm³/s at 300°F (422.2 K). Calculate the entering concentration of A, C_{A0} , and the entering molar flow rate, F_{A0} . The ideal gas constant is

$$R = 0.082 \text{ dm}^3 \cdot \text{atm} / \text{mol} \cdot \text{K} \quad (\text{Appendix B})$$

Solution

We recall that for an ideal gas:

$$C_{A0} = \frac{P_{A0}}{RT_0} \approx \frac{y_{A0} P_0}{RT_0} \quad (\text{E2-1.1})$$

where $P_0 = 10 \text{ atm}$

$y_{A0} = 0.5$

P_{A0} = initial partial pressure = $y_{A0} P_0 = (0.5)(10 \text{ atm}) = 5 \text{ atm}$

T_0 = initial temperature = 300°F = 149°C = 422.2 K

$$R = \frac{0.82 \text{ dm}^3 \cdot \text{atm}}{\text{mol} \cdot \text{K}}$$

We could also solve for the partial pressure in terms of the concentration

$$P_{A0} = C_{A0} R T_0 \quad (\text{E2-1.2})$$

Substituting values in Equation (E2-1.1) yields

$$C_{A0} \approx \frac{0.5(10 \text{ atm})}{0.082 \text{ dm}^3 \cdot \text{atm} / \text{mol} \cdot \text{K}(422.2 \text{ K})} = 0.14442 \frac{\text{mol}}{\text{dm}^3}$$

Keeping only the significant figures gives us

$$C_{A0} \approx 0.144 \text{ mol/dm}^3 = 0.144 \text{ kmol/m}^3 = 0.144 \text{ mol/L}$$

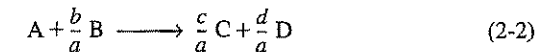
The entering molar flow rate, F_{A0} , is just the product of the entering concentration, C_{A0} , and the entering volumetric flow rate, v_0 :

$$F_{A0} = C_{A0} v_0 = (0.14442 \text{ mol/dm}^3)(6.0 \text{ dm}^3/\text{s}) = 0.867 \text{ mol/s}$$

We will use this value of F_{A0} together with either Table 2-2 or Figure 2-1 to size a number of reactor schemes in Examples 2-2 through 2-5.

Now that we have a relationship [Equation (2-10)] between the molar flow rate and conversion, it is possible to express the design equations (i.e., mole balances) in terms of conversion for the *flow* reactors examined in Chapter 1.

CSTR or Backmix Reactor. The equation resulting from a mole balance on species A for the reaction



occurring in a CSTR was given by Equation (1-6), which can be arranged to

$$F_{A0} - F_A = -r_A V \quad (2-11)$$

We now substitute for the exiting molar flow rate of A, F_A , in terms of the conversion X and the entering molar flow rate, F_{A0} , by using Equation (2-10) in the form

$$F_{A0} - F_A = F_{A0} X$$

and combining it with Equation (2-11) to give

$$F_{A0} X = -r_A V \quad (2-12)$$

We can rearrange Equation (2-12) to determine the CSTR volume necessary to achieve a specified conversion X .

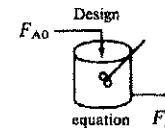
$$V = \frac{F_{A0} X}{(-r_A)_{\text{exit}}} \quad (2-13)$$

Since the exit composition from the reactor is identical to the composition inside the reactor, the rate of reaction is evaluated at the exit conditions.

Tubular Flow Reactor (PFR). After multiplying both sides of the tubular reactor design equation (1-10) by -1 , we express the mole balance equation for species A in the reaction given by Equation (2-2) as

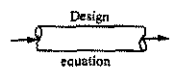
$$\frac{-dF_A}{dV} = -r_A \quad (2-14)$$

For a flow system, F_A has previously been given in terms of the entering molar flow rate F_{A0} and the conversion X :



$$F_A = F_{A0} - F_{A0}X \quad (2-10)$$

Substituting Equation (2-10) into (2-14) gives the differential form of the design equation for a plug-flow reactor:



$$F_{A0} \frac{dX}{dV} = -r_A \quad (2-15)$$

We now separate the variables and integrate with the limit $V = 0$ when $X = 0$ to obtain the plug-flow reactor volume necessary to achieve a specified conversion X :

$$V = F_{A0} \int_0^X \frac{dX}{-r_A} \quad (2-16)$$

To carry out the integrations in the batch and plug-flow reactor design equations (2-9) and (2-16), as well as to evaluate the CSTR design equation (2-13), we need to know how the reaction rate $-r_A$ varies with the concentration (hence conversion) of the reacting species. This relationship between reaction rate and concentration is developed in Chapter 3.

Packed-Bed Reactor. The derivation of the differential and integral forms of the design equations for a packed-bed reactor are analogous to those for a PFR [cf. Equations (2-15) and (2-16)]. That is, substituting for F_A in Equation (1-11) gives

PBR design
equation

$$F_{A0} \frac{dX}{dW} = -r'_A \quad (2-17)$$

The differential form of the design equation [i.e., Equation (2-17)] *must* be used when analyzing reactors that have a pressure drop along the length of the reactor. We discuss pressure drop in packed-bed reactors in Chapter 4.

Integrating with the limits $W = 0$ at $X = 0$ gives



$$W = F_{A0} \int_0^X \frac{dX}{-r'_A} \quad (2-18)$$

Equation (2-18) can be used to determine the catalyst weight W necessary to achieve a conversion X when the total pressure remains constant.

2.3 Applications of the Design Equations for Continuous-Flow Reactors

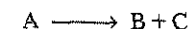
The rate of disappearance of A, $-r_A$, is almost always a function of the concentrations of the various species present. When a single reaction is occurring,

each of the concentrations can be expressed as a function of the conversion X (see Chapter 3); consequently, $-r_A$ can be expressed as a function of X .

A particularly simple functional dependence, yet one that occurs on many occasions, is $-r_A = kC_{A0}(1 - X)$. For this dependence, a plot of the reciprocal rate of reaction ($1/-r_A$) as a function of conversion yields a curve similar to the one shown in Figure 2-1, where

$$\frac{1}{-r_A} = \frac{1}{kC_{A0}} \left(\frac{1}{1 - X} \right)$$

To illustrate the design of a series of reactors, we consider the isothermal gas-phase decomposition reaction



The laboratory measurements given in Table 2-1 show the chemical reaction rate as a function of conversion. The temperature was 300°F (422.2 K), the total pressure 10 atm (1013 kPa), and the initial charge an equimolar mixture of A and inerts.

TABLE 2-1 RAW DATA

X	$-r_A$ (mol/dm ³ · s)
0.0	0.0053
0.1	0.0052
0.2	0.0050
0.3	0.0045
0.4	0.0040
0.5	0.0033
0.6	0.0025
0.7	0.0018
0.8	0.00125
0.85	0.00100

If we know $-r_A$ as a function of X , we can size any isothermal reaction system.

The rate data in Table 2-1 have been converted to reciprocal rates, $1/-r_A$ in Table 2-2, which are now used to arrive at the desired plot of $1/-r_A$ as a function of X , shown in Figure 2-1. We will use this figure to illustrate how one can size each of the reactors in a number of different reactor sequences. The volumetric feed to each reactor sequence will be 6.0 dm³/s. First, though, some initial conditions should be evaluated. If a reaction is carried out isothermally, the rate is usually greatest at the start of the reaction when the concentration of reactant is greatest [i.e., when there is negligible conversion ($X = 0$)]. Hence $(1/-r_A)$ will be small. Near the end of the reaction, when the reactant concentration is small (i.e., the conversion is large), the reaction rate will be small. Consequently, $(1/-r_A)$ is large. For irreversible reactions of greater than zero-order,

TABLE 2-2 PROCESSED DATA

X	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.85
$-r_A$	0.0053	0.0052	0.0050	0.0045	0.0040	0.0033	0.0025	0.0018	0.00125	0.001
$1/-r_A$	189	192	200	222	250	303	400	556	800	1000

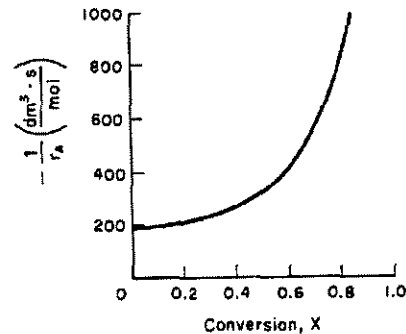
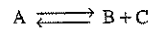


Figure 2-1 Processed Data.



$$-\frac{1}{r_A} \rightarrow \infty \text{ as } X \rightarrow 1$$

For reversible reactions in which the equilibrium conversion is X_e ,



$$-\frac{1}{r_A} \rightarrow \infty \text{ as } X \rightarrow X_e$$

These characteristics are illustrated in Figure 2-1. The majority of reactions exhibit qualitatively similar curves for isothermal operation.

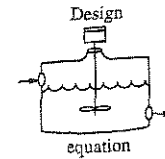
Example 2-2 Sizing a CSTR

(a) Using the data in either Table 2-2 or Figure 2-1, calculate the volume necessary to achieve 80% conversion in a CSTR. (b) Shade the area in Figure 2-1 which when multiplied by F_{A0} would give the volume of a CSTR necessary to achieve 80% conversion (i.e., $X = 0.8$).

Solution

From Example 2-1, knowing the entering conditions $v_0 = 6 \text{ dm}^3/\text{s}$, $P_0 = 10 \text{ atm}$, $y_{A0} = 0.5$, $T_0 = 422.2 \text{ K}$, we can use the ideal gas law to calculate the entering molar flow rate of A, i.e.,

$$F_{A0} = C_{A0}v_0 = \frac{y_{A0}P_0}{RT_0}v_0 = \frac{(0.5)(1013 \text{ kPa}) \cdot 6 \text{ dm}^3/\text{s}}{[8.314 \text{ kPa dm}^3/(\text{mol})(\text{K})](422.2 \text{ K})} = 0.867 \text{ mol/s}$$



(a) Equation (2-13) gives the volume of a CSTR as a function of F_{A0} , X , and $-r_A$:

$$V = \frac{F_{A0}X}{-r_A} \quad (2-13)$$

In a CSTR, the composition, temperature, and conversion of the effluent stream are identical to that of the fluid within the reactor, since perfect mixing is assumed. Therefore, we need to find the value of $-r_A$ (or reciprocal thereof) at $X = 0.8$. From either Table 2-2 or Figure 2-1 we see that when $X = 0.8$, then

$$1/-r_A = 800 \frac{\text{dm}^3 \cdot \text{s}}{\text{mol}}$$

Substitution into Equation (2-13) gives

$$V = 0.867 \frac{\text{mol}}{\text{s}} \left(\frac{800 \text{ dm}^3 \cdot \text{s}}{\text{mol}} \right) (0.8) = 554.9 \text{ dm}^3 = 554.9 \text{ L} \quad (\text{E2-2.1})$$

(b) Shade the area in Figure 2-1 which when multiplied by F_{A0} yields the CSTR volume. Rearranging Equation (2-13) gives

$$V = F_{A0} \left(\frac{1}{-r_A} \right) X \quad (2-13)$$

$$\frac{V}{F_{A0}} = \left[\frac{1}{-r_A} \right]_{X=0.8} (0.8) \quad (\text{E2-2.2})$$

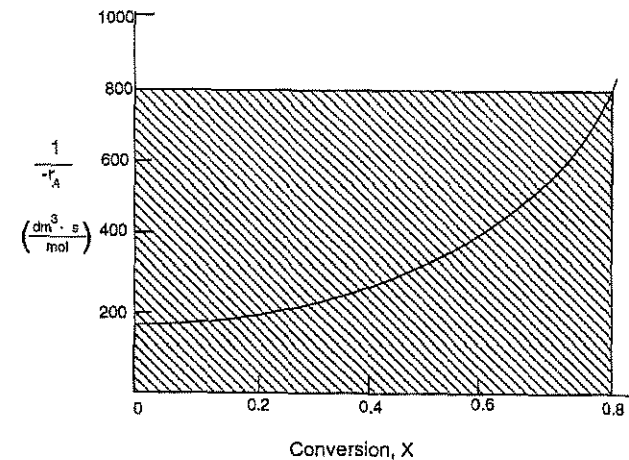


Figure E2-2.1 Levenspiel CSTR plot.

In Figure E2-2.1 the value of V/F_{A0} is equal to the area of a rectangle with a height $1/-r_A = 800 \text{ dm}^3 \cdot \text{s}/\text{mol}$ and a base $X = 0.8$. This rectangle is shaded in the figure. To calculate the reactor volume, we multiply the area of the rectangle by F_{A0} .

Plots of $1/-r_A$ vs. X are sometimes referred to as Levenspiel plots (after Octave Levenspiel)

$$V = 0.867 \frac{\text{mol}}{\text{s}} \left[800 \frac{\text{dm}^3 \cdot \text{s}}{\text{mol}} (0.8) \right] = 554.9 \text{ dm}^3$$

The CSTR volume necessary to achieve 80% conversion at the specified temperature and pressure is 555 dm³.

Example 2-3 Sizing a PFR

The reaction described by the data in Tables 2-1 and 2-2 is to be carried out in a PFR. The entering molar flow rate is 5 mol/s. Calculate the reactor volume necessary to achieve 80% conversion in a PFR. (a) First, use one of the integration formulas given in Appendix A.4 to determine the PFR reactor volume. (b) Next, shade the area in Figure 2-1 which when multiplied by F_{A0} would give the PFR volume. (c) Make a qualitative sketch of the conversion, X , and the rate of reaction, $-r_A$, down the length (volume) of the reactor.

Solution

(a) For the PFR, the differential form of the mole balance is

$$F_{A0} \frac{dX}{dV} = -r_A \quad (2-15)$$

Rearranging and integrating gives

$$V = F_{A0} \int_0^X \frac{dX}{-r_A} \quad (2-16)$$

For 80% conversion, we will use the five-point quadratic formula with $\Delta X = 0.2$.

$$\begin{aligned} V &= F_{A0} \int_0^X \frac{dX}{-r_A} \\ &= F_{A0} \frac{\Delta X}{3} \left[\frac{1}{-r_A(X=0)} + \frac{4}{-r_A(0.2)} + \frac{2}{-r_A(0.4)} + \frac{4}{-r_A(0.6)} + \frac{1}{-r_A(0.8)} \right] \end{aligned}$$

Using values of $1/-r_A$ in Table 2-2 yields

$$\begin{aligned} V &= (0.867 \text{ mol/s})(0.2/3)[189 + 4(200) + 2(250) + 4(400) + (800)] \frac{\text{s} \cdot \text{dm}^3}{\text{mol}} \\ &= (0.867 \text{ mol/s})(259.3 \text{ s} \cdot \text{dm}^3/\text{mol}) \\ &= 225 \text{ dm}^3 \end{aligned}$$

(b) The integral in Equation (2-16) can be evaluated for the area under the curve of a plot of $(1/-r_A)$ versus X .

$$\frac{V}{F_{A0}} = \int_0^{0.8} \frac{dX}{-r_A} = \text{area under the curve between } X=0 \text{ and } X=0.8 \text{ (see appropriate shaded area in Figure E2-3.1)}$$

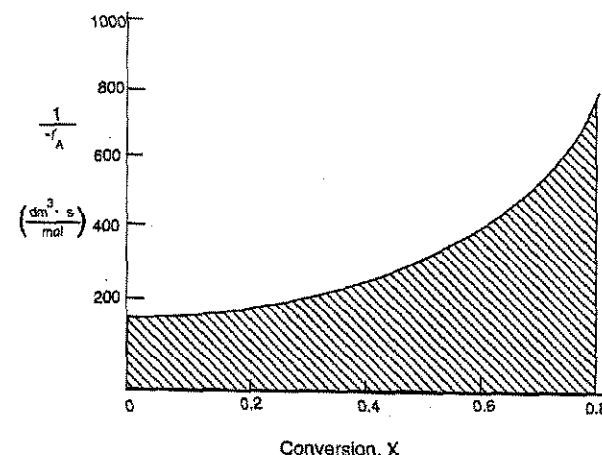


Figure E2-3.1 Levenspiel PFR plot.

The product of this area and F_{A0} will give the tubular reactor volume necessary to achieve the specified conversion of A. For 80% conversion, the shaded area is roughly equal to 260 dm³·(s/mol). The tubular reactor volume can be determined by multiplying this area [in dm³·(s/mol)] by F_{A0} (mol/s). Consequently, for an entering molar flow rate of 0.867 mol/s the PFR volume necessary to achieve 80% conversion is 225 dm³.

(c) Sketch $-r_A$ and X down the length of the reactor. We know that as we proceed down the reactor and more and more of the reactant is consumed, the concentration of reactant decreases, as does the rate of disappearance of A. However, the conversion increases as more and more reactant is converted to product. For $X = 0.2$ we calculate the corresponding reactor volume using Simpson's rule with $\Delta X = 0.1$.

$$\begin{aligned} V &= F_{A0} \int_0^{0.2} \frac{dX}{-r_A} = F_{A0} \frac{\Delta X}{3} \left[\frac{1}{-r_A(X=0)} + \frac{4}{-r_A(X=0.1)} + \frac{1}{-r_A(X=0.2)} \right] \\ &= 0.867 \frac{\text{mol}}{\text{s}} \left[\frac{0.1}{3} [189 + 4(192) + 200] \right] \frac{\text{dm}^3}{\text{mol} \cdot \text{s}} \\ &= 33.4 \text{ dm}^3 \end{aligned}$$

For $X = 0.4$, we can again use Simpson's rule with $\Delta X = 0.2$:

$$\begin{aligned} V &= F_{A0} \frac{\Delta X}{3} \left[\frac{1}{-r_A(X=0)} + \frac{4}{-r_A(X=0.2)} + \frac{1}{-r_A(X=0.4)} \right] \\ &= 0.867 \frac{\text{mol}}{\text{s}} \left[\frac{0.2}{3} [189 + 4(200) + 250] \right] \frac{\text{dm}^3}{\text{mol} \cdot \text{s}} \\ &= 71.6 \text{ dm}^3 \end{aligned}$$

We can continue in this manner to arrive at Table E2-3.1.

TABLE E2-3.1. CONVERSION PROFILE					
$V(\text{dm}^3)$	0	33.4	71.6	126	225
X	0	0.2	0.4	0.6	0.8
$-r_A \left(\frac{\text{mol}}{\text{dm}^3 \cdot \text{s}} \right)$	0.0053	0.005	0.004	0.0025	0.00125

which is shown in Figure E2-3.2.

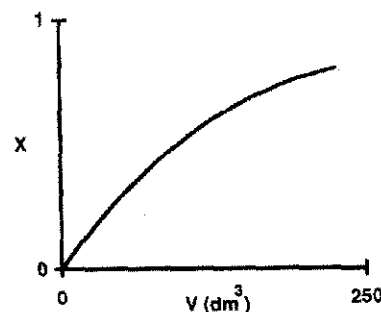


Figure E2-3.2 Conversion profile.

Rather than using Simpson's rule we could have used the data in Table 2-2 to fit $-r_A(X)$ to a polynomial and then used POLYMATH to integrate the design equation to obtain the conversion profile.

Example 2-4 Comparing CSTR and PFR Sizes

It is interesting to compare the volumes of a CSTR and a plug-flow reactor (PFR) required for the same job. To do this we shall use the data in Figure 2-1 to learn which reactor would require the smaller volume to achieve a conversion of 60%: a CSTR or a PFR. The feed conditions are the same in both cases. The entering molar flow rate is 5 mol/s.

Solution

For the CSTR:

$$\frac{V}{F_{A0}} = \left(\frac{1}{-r_A} \right) X = (400)(0.6) = 240 \frac{\text{dm}^3 \cdot \text{s}}{\text{mol}}$$

This is also the area of the rectangle with vertices $(X, 1/-r_A)$ of $(0, 0)$, $(0, 400)$, $(0.6, 400)$, and $(0.6, 0)$. The CSTR volume necessary to achieve 60% conversion is

$$V = \left(\frac{5 \text{ mol}}{\text{s}} \right) \left(\frac{240 \text{ dm}^3 \cdot \text{s}}{\text{mol}} \right) = 1200 \text{ dm}^3$$

For the plug-flow (tubular) reactor:

$$F_{A0} \frac{dX}{dV} = -r_A$$

Integrating and rearranging Equation (2-15) yields

$$\begin{aligned} \frac{V}{F_{A0}} &= \int_0^{0.6} \frac{dX}{-r_A} = \frac{\Delta X}{3} \left[\frac{1}{-r_A(0.0)} + \frac{4}{-r_A(0.3)} + \frac{1}{-r_A(0.6)} \right] \\ &= \frac{0.3}{3} \times [189 + 4(222) + 400] \\ &= 148 \frac{\text{dm}^3 \cdot \text{s}}{\text{mol}} \end{aligned}$$

The PFR volume necessary to achieve 60% conversion is

$$V = \left(\frac{5 \text{ mol}}{\text{s}} \right) \left(148 \frac{\text{dm}^3 \cdot \text{s}}{\text{mol}} \right) = 740 \text{ dm}^3$$

For the same flow rate F_{A0} the plug-flow reactor requires a smaller volume than the CSTR to achieve a conversion of 60%. This comparison can be seen in Figure E2-4.1. For isothermal reactions of greater than zero order, the PFR will always require a smaller volume than the CSTR to achieve the same conversion.

Generally, the isothermal tubular reactor volume is smaller than the CSTR for the same conversion

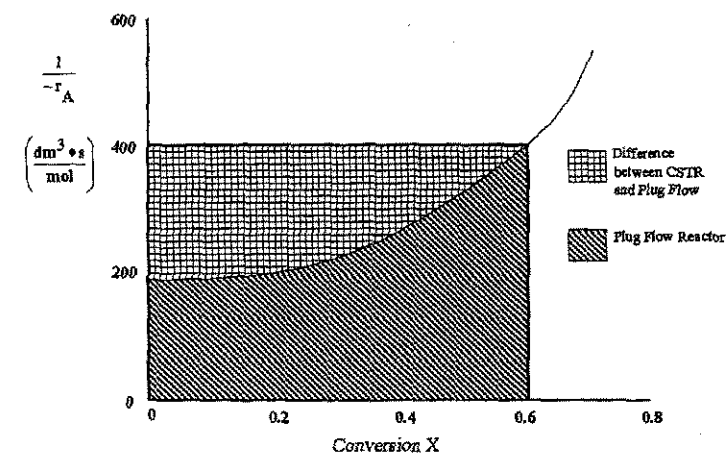


Figure E2-4.1 Levenspiel plot comparing CSTR and PFR size.

2.4 Reactors in Series

Many times reactors are connected in series so that the exit stream of one reactor is the feed stream for another reactor. When this arrangement is used it is often possible to speed calculations by defining conversion in terms of location at a point downstream rather than with respect to any single reactor. That is, the conversion X is the *total number of moles of A that have reacted up to that point per mole of A fed to the first reactor*. However, this definition can only be used provided that there are no side streams withdrawn and the feed stream enters only the first reactor in the series.

As an example, the relationships between conversion and molar flow rates for the reactor sequence shown in Figure 2-2 are given by the following equations:

$$F_{A1} = F_{A0} - F_{A0}X_1$$

$$F_{A2} = F_{A0} - F_{A0}X_2$$

$$F_{A3} = F_{A0} - F_{A0}X_3$$

where

$$X_2 = \frac{\text{total moles of A reacted up to point 2}}{\text{mole of A fed to first reactor}}$$

Similar definitions exist for X_1 and X_3 .

The volume V_1 is given by Equation (2-16):

Reactor 1

$$V_1 = F_{A0} \int_0^{X_1} \frac{dX}{-r_A}$$

A mole balance on species A for the CSTR in the middle gives

$$\begin{aligned} \text{in} - \text{out} + \text{generation} &= 0 \\ F_{A1} - F_{A2} + r_{A2}V_2 &= 0 \end{aligned}$$

Rearranging gives us

$$V_2 = \frac{F_{A1} - F_{A2}}{-r_{A2}}$$

$-r_{A2}$ is evaluated at X_2 for the CSTR in this series arrangement

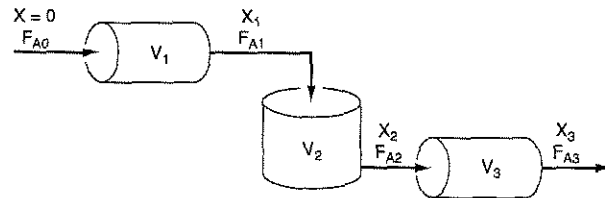


Figure 2-2 PFR-CSTR-PFR in series.

The corresponding rate of reaction $-r_{A2}$ is evaluated at the conversion X_2 . Substituting for F_{A1} and F_{A2} yields

Reactor 2

$$V_2 = \frac{F_{A0}(X_2 - X_1)}{-r_{A2}} \quad (2-19)$$

The volume for the third reactor, V_3 , is found by integrating Equation (2-15) between the limits X_2 and X_3 :

Reactor 3

$$V_3 = F_{A0} \int_{X_2}^{X_3} \frac{dX}{-r_A}$$

To demonstrate these ideas, let us consider three different schemes of reactors in series: two CSTRs, two PFRs, and a PFR connected to a CSTR. To size these reactors we shall use laboratory data that give the reaction rate at different conversions. The reactors will operate at the same temperature and pressure as were used in obtaining the laboratory data.

We will now use the value of F_{A0} calculated in Example 2-1 together with Figure 2-1 to size each of the reactors for the three reactor schemes. The first scheme to be considered is the two CSTRs in series shown in Figure 2-3. For the first reactor in which the rate of disappearance of A is $-r_{A1}$ at conversion X_1 , the volume necessary to achieve the conversion X_1 is

$$V_1 = F_{A0} \left(\frac{1}{-r_{A1}} \right) X_1$$

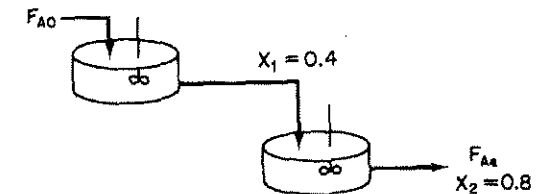


Figure 2-3 Two CSTRs in series.

In the second reactor, the rate of disappearance of A, $-r_{A2}$, is evaluated and the conversion is that of the exit stream of reactor 2, X_2 . The volume necessary to increase the conversion in reactor 2 from X_1 to X_2 was derived previously and is given by Equation (2-19):

$$V_2 = \frac{F_{A0}(X_2 - X_1)}{-r_{A2}} \quad (2-19)$$

Example 2-5 Comparing Volumes for CSTRs in Series

For the two CSTRs in series, 40% conversion is achieved in the first reactor. What is the total volume of the two reactors necessary for 80% overall conversion of the species A entering reactor 1? (If F_{A2} is the molar flow rate of A exiting from the last reactor in the sequence, $F_{A2} = 0.2F_{A0}$.)

Solution

$$F_{A0} = 0.867 \text{ mol/s}$$

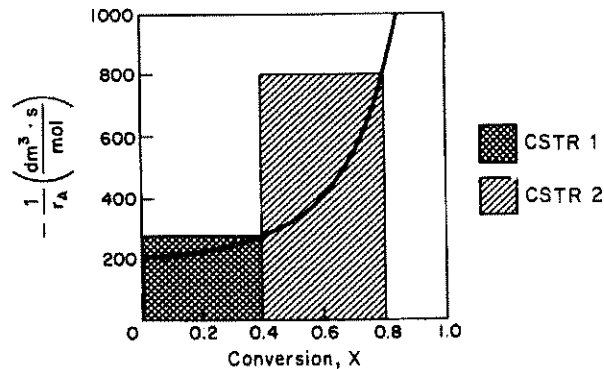


Figure E2-5.1 Levenspiel plot for two CSTRs in series.

For reactor 1 we observe from either Table 2-2 or Figure E2-5.1 that when $X = 0.4$, then

$$\frac{1}{-r_{A1}} = 250 \text{ dm}^3 \cdot \text{s/mol}$$

Then

$$V_1 = F_{A0} \left(\frac{1}{-r_{A1}} \right) X = 0.867 \left(\frac{1}{-r_{A1}} \right) (0.4) = (0.867)(250)(0.4)$$

$$V_1 = 86.7 \text{ dm}^3 \text{ (liters)}$$

For reactor 2, when $X_2 = 0.8$, then $(1/-r_A) = 800 \text{ dm}^3 \cdot \text{s/mol}$, and

$$\begin{aligned} V_2 &= F_{A0} \left(\frac{1}{-r_{A2}} \right) (X_2 - X_1) \\ &= \left(0.867 \frac{\text{mol}}{\text{s}} \right) \left(800 \frac{\text{dm}^3 \cdot \text{s}}{\text{mol}} \right) (0.8 - 0.4) \\ &= 277.4 \text{ dm}^3 \text{ (liters)} \end{aligned}$$

To achieve the same overall conversion, the total volume for two CSTRs in series is less than that required for one CSTR

Note again that for CSTRs in series the rate $-r_{A1}$ is evaluated at a conversion of 0.4 and rate $-r_{A2}$ is evaluated at a conversion of 0.8. The total volume is

$$V = V_1 + V_2 = 364 \text{ dm}^3 \text{ (liters)}$$

The volume necessary to achieve 80% conversion in one CSTR is

$$V = F_{A0} \left(\frac{1}{-r_A} \right) X = (0.867)(800)(0.8) = 555 \text{ dm}^3 \text{ (liters)}$$

Notice in Example 2-5 that the sum of the two CSTR reactor volumes (364 L) in series is less than the volume of one CSTR (555 L) to achieve the same conversion. This case does not hold true for two plug-flow reactors connected in series as shown in Figure 2-4. We can see from Figure 2-5 and from the equation

$$\int_0^{X_2} \frac{dX}{-r_A} = \int_0^{X_1} \frac{dX}{-r_A} + \int_{X_1}^{X_2} \frac{dX}{-r_A}$$

that it is immaterial whether you place two plug-flow reactors in series or have one continuous plug-flow reactor; the total reactor volume required to achieve the same conversion is identical.

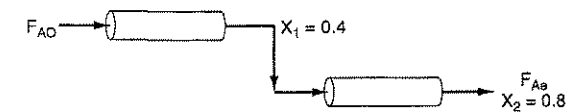


Figure 2-4 Two PFRs in series.

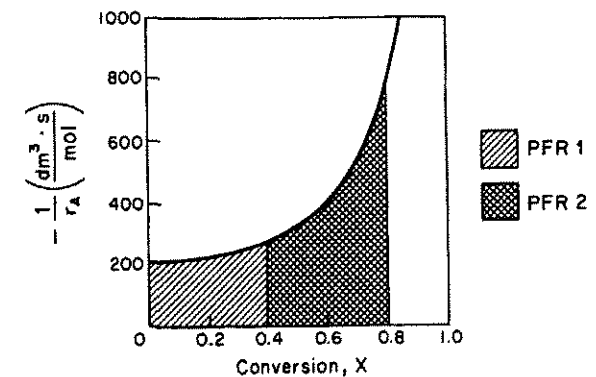


Figure 2-5 Levenspiel plot for two PFRs in series.

Example 2-6 Sizing Plug-Flow Reactors in Series

Using either the data in Table 2-2 or Figure 2-5, calculate the reactor volumes V_1 and V_2 for the plug-flow sequence shown in Figure 2-4 when the intermediate conversion is 40% and the final conversion is 80%. The entering molar flow rate is the same as in the previous examples, 0.867 mol/s.

Solution

In addition to graphical integration we could have used numerical methods to size the plug-flow reactors. In this example, we shall use Simpson's rule (see Appendix A.4) to evaluate the integrals.

$$\int_{X_0}^{X_2} f(X) dX = \frac{\Delta X}{3} [f(X_0) + 4f(X_1) + f(X_2)] \quad (\text{A-23})$$

For the first reactor, $X_0 = 0$, $X_1 = 0.2$, $X_2 = 0.4$, and $\Delta X = 0.2$,

$$V_1 = F_{A0} \int_0^{0.4} \frac{dX}{-r_A} = F_{A0} \frac{\Delta X}{3} \left[\frac{1}{-r_A(0)} + 4 \frac{1}{-r_A(0.2)} + \frac{1}{-r_A(0.4)} \right] \quad (\text{E2-6.1})$$

Selecting the appropriate values from Table 2-2, we have

$$\begin{aligned} V_1 &= (0.867 \text{ mol/s}) \left(\frac{0.2}{3} \right) [189 + 4(200) + 250] \text{ L} \cdot \text{s/mol} \\ &= 71.6 \text{ L} = 71.6 \text{ dm}^3 \end{aligned}$$

For the second reactor,

$$\begin{aligned} V_2 &= F_{A0} \int_{0.4}^{0.8} \frac{dX}{-r_A} \\ &= F_{A0} \frac{\Delta X}{3} \left[\frac{1}{-r_A(0.4)} + 4 \frac{1}{-r_A(0.6)} + \frac{1}{-r_A(0.8)} \right] \quad (\text{E2-6.2}) \\ &= (0.867 \text{ mol/s}) \left(\frac{0.2}{3} \right) [250 + 4(400) + 800] \text{ L} \cdot \text{s/mol} \\ &= 153 \text{ L} = 153 \text{ dm}^3 \end{aligned}$$

The total volume is then

$$V = V_1 + V_2 = 225 \text{ L} = 225 \text{ dm}^3$$

The final sequence we shall consider is a CSTR and plug-flow reactor in series. There are two ways in which this sequence can be arranged (Figure

2-6). If the size of each reactor is fixed, a different final conversion, X_2 , will be achieved, depending on whether the CSTR, or the plug-flow reactor is placed first. If the intermediate and exit conversions are specified, the reactor volumes as well as their sums can be different for different sequencing. Figure 2-7 shows an actual system of two CSTRs and a PFR in series.

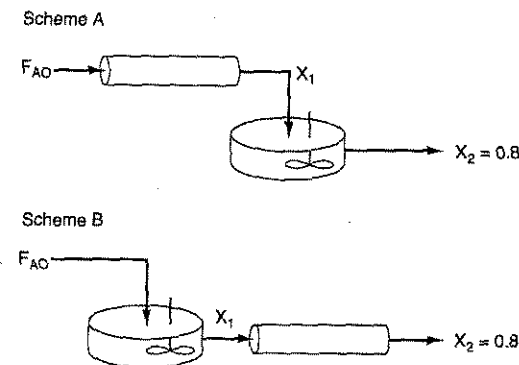


Figure 2-6

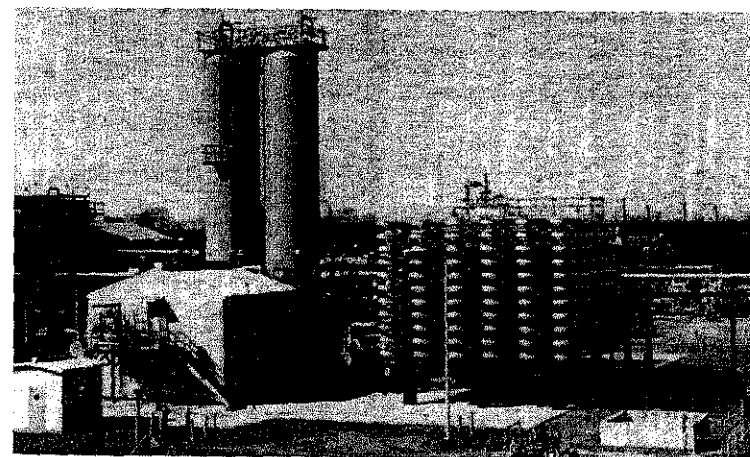


Figure 2-7 Dimersol G (an organometallic catalyst) unit (two CSTRs and one tubular reactor in series) to dimerize propylene into isohexanes. Institut Français du Pétrole process. [Photo courtesy of Editions Technip (Institut Français du Pétrole).]

Example 2-7 Comparing the Order of Sequencing Reactors

Calculate the individual reactor volume as well as the total reactor volume for each scheme in Figure 2-6 for the reaction data given in Table 2-2 when the intermediate conversion is 50% and $F_{A0} = 0.867$ mol/s.

Solution

We again use Figure 2-1 to arrive at Figure E2-7.1 and evaluate the design integrals.

Scheme A

Plug flow: $F_{A0} \frac{dX}{dV} = -r_A$

Integrating between $X = 0$ and $X = 0.5$ yields

$$\begin{aligned} V_1 &= F_{A0} \int_0^{0.5} \frac{dX}{-r_A} = F_{A0} \left[\frac{\Delta X}{3} [f(X_0) + 4f(X_1) + f(X_2)] \right] \\ &= F_{A0} \frac{\Delta X}{3} \left[\frac{1}{-r_A(0)} + \frac{4}{-r_A(0.25)} + \frac{1}{-r_A(0.5)} \right] \\ &= F_{A0} \frac{0.25}{3} [189 + 4 \times 211 + 303] \\ &= (0.867)(111) \\ &= 97 \text{ dm}^3 \text{ (liters)} \end{aligned}$$

$$\begin{aligned} \text{CSTR: } V_2 &= F_{A0} \frac{X_2 - X_1}{-r_{A2}} = 0.867(0.8 - 0.5)(800) = 208 \text{ dm}^3 \\ V_{\text{total}} &= V_1 + V_2 = 305 \text{ dm}^3 \end{aligned}$$

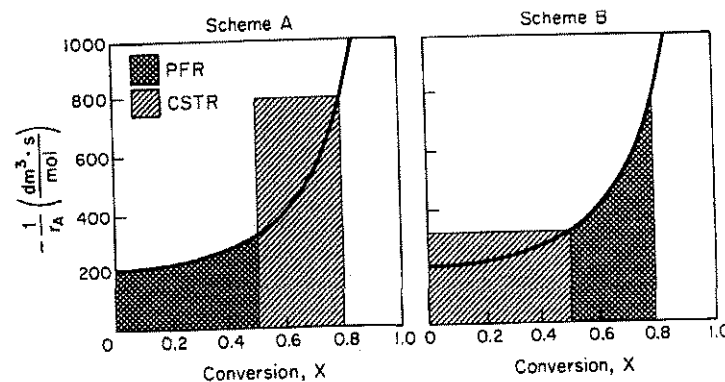


Figure E2-7.1

Scheme B

$$\text{CSTR: } V_1 = \frac{F_{A0} X_1}{-r_{A1}} = 0.867(0.5)(303) = 131.4 \text{ dm}^3$$

$$\text{PFR: } V_2 = F_{A0} \int_{0.5}^{0.8} \frac{dX}{-r_A} = 0.867(151) = 130.9 \text{ dm}^3$$

$$V_{\text{total}} = 262 \text{ dm}^3 \text{ (liters)}$$

Scheme B will give the smaller total reactor volume for an intermediate conversion of 50%. This result is shown in Figure E2-7.1. However, as is seen in Problem P2-3, the relative sizes of the reactors depend on the intermediate conversion. Compare your results in Example 2-7 with those in Problem P2-3.

The previous examples show that if we know the molar flow rate to the reactor and the reaction rate as a function of conversion, then we can calculate the reactor volume necessary to achieve a specified conversion. The reaction rate does not depend on conversion alone, however. It is also affected by the initial concentrations of the reactants, the temperature, and the pressure. Consequently, the experimental data obtained in the laboratory and presented in Table 2-1 as $-r_A$ for given values of X are useful only in the design of full-scale reactors that are to be operated at the same conditions as the laboratory experiments (temperature, pressure, initial reactant concentrations). This conditional relationship is generally true; i.e., to use laboratory data directly for sizing reactors, the laboratory and full-scale operating conditions must be identical. Usually, such circumstances are seldom encountered and we must revert to the methods described in Chapter 3 to obtain $-r_A$ as a function of X .

However, it is important for the reader to realize that if the rate of reaction is available solely as a function of conversion, $-r_A = f(X)$, or if it can be generated by some intermediate calculation, one can design a variety of reactors or combination of reactors.

Finally, let's consider approximating a PFR with a number of small, equal-volume CSTRs of V_i in series (Figure 2-8). We want to compare the total

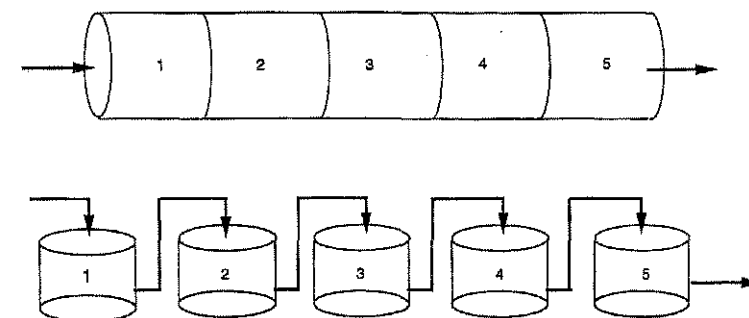


Figure 2-8 Modeling a PFR with CSTRs in series.

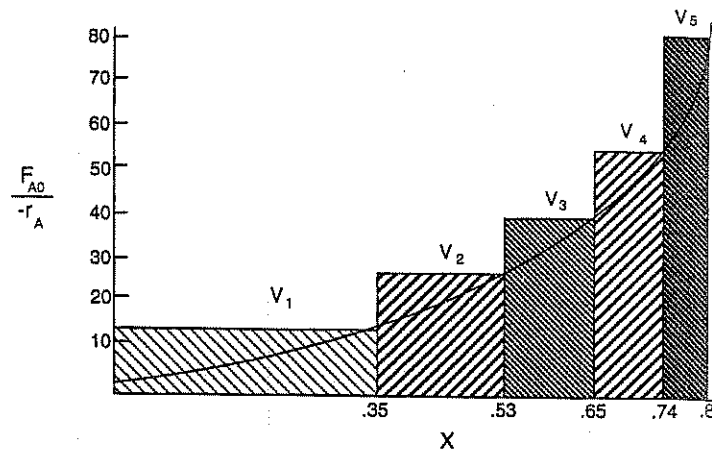


Figure 2-9 Levenspiel plot showing comparison of CSTRs in series with one PFR.

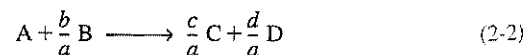
volume of all the CSTRs with the volume of one plug-flow reactor for the same conversion, say 80%. From Figure 2-9 we note a very important observation! The total volume to achieve 80% conversion for five CSTRs of equal volume in series is roughly the same as the volume of a PFR. As we make the volume of each CSTR smaller and increase the number of CSTRs, the total volume of the CSTRs and the PFR will become identical. *That is, we can model a PFR as a number of CSTRs in series.* This concept will be used later in a number of situations, such as modeling catalyst decay in packed-bed reactors or transit heat effects in PFRs.

Ordinarily, laboratory data are used to formulate a rate law, and then the reaction rate-conversion functional dependence is determined using the rate law. Preceding sections show that with the reaction rate-conversion relationship, different reactor schemes can readily be sized. In Chapter 3 we show how we obtain this relationship between reaction rate and conversion from rate law and reaction stoichiometry.

2.5 Some Further Definitions

Before proceeding to Chapter 3, some terms and equations commonly used in reaction engineering need to be defined. We also consider the special case of the plug-flow design equation when the volumetric flow rate is constant.

Relative Rates of Reaction. The relative rates of reaction of the various species involved in a reaction can be obtained from the ratio of stoichiometric coefficients. For Reaction (2-2),



we see that for every mole of A that is consumed, c/a moles of C appear. In other words,

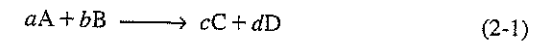
$$\text{rate of formation of C} = \frac{c}{a} (\text{rate of disappearance of A})$$

$$r_C = \frac{c}{a} (-r_A) = -\frac{c}{a} r_A$$

Similarly, the relationship between the rate of formation of C and D is

$$r_C = \frac{c}{d} r_D$$

The relationship can be expressed directly from the stoichiometry of the reaction,



for which

$$\frac{-r_A}{a} = \frac{-r_B}{b} = \frac{r_C}{c} = \frac{r_D}{d} \quad (2-20)$$

Remember this very important relationship for the relative rates of reaction.

Space Time. The space time, τ , is obtained by dividing reactor volume by the volumetric flow rate entering the reactor:

$$\tau \equiv \frac{V}{v_0} \quad (2-21)$$

The space time is the time necessary to process one reactor volume of fluid based on entrance conditions. For example, consider the tubular reactor shown in Figure 2-10, which is 20 m long and 0.2 m³ in volume. The dashed line in Figure 2-10 represents 0.2 m³ of fluid directly upstream of the reactor. The time it takes for this fluid to enter the reactor completely is the space time. It is also called the *holding time* or *mean residence time*.

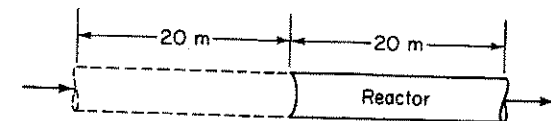
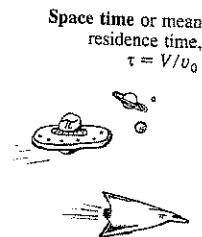


Figure 2-10

If both sides of the plug-flow reactor design equation (2-16) are divided by the entering volumetric flow rate and then the left-hand side is put in terms of space time, the equation takes the form

$$\tau = C_{A0} \int_0^X \frac{dX}{-r_A}$$

The space velocity (SV), which is defined as

$$SV = \frac{v_0}{V} \quad SV = \frac{1}{\tau} \quad (2-22)$$

might at first sight be regarded as the reciprocal of the space time. However, there is a difference in the two quantities' definitions. For the space time, the entering volumetric flow rate is measured at the entrance condition, while for the space velocity other conditions are often used. The two space velocities commonly used in industry are the liquid hourly and gas hourly space velocities, LHSV and GHSV, respectively. The v_0 in the LHSV is frequently measured as that of a liquid at 60 or 75°F, even though the feed to the reactor may be a vapor at some higher temperature. The v_0 in the GHSV is normally measured at standard temperature and pressure (STP).

For reactions in which the rate depends only on the concentration of one species [i.e., $-r_A = f(C_A)$], it is usually convenient to report $-r_A$ as a function of concentration rather than conversion. We can rewrite the design equation for a plug-flow reactor [Equation (2-16)] in terms of the concentration, C_A , rather than in terms of conversion for the special case when $v = v_0$.

$$V = F_{A0} \int_0^X \frac{dX}{-r_A} \quad (2-16)$$

$$F_{A0} = v_0 C_{A0} \quad (2-23)$$

Rearranging Equation (2-10) gives us

$$X = \frac{F_{A0} - F_A}{F_{A0}} \quad (2-24)$$

For the *special case* when $v = v_0$,

$$X = \frac{F_{A0} - F_A}{F_{A0}} = \frac{C_{A0}v_0 - C_A v}{C_{A0}v_0} = \frac{C_{A0} - C_A}{C_{A0}}$$

$$\text{when } X = 0, C_A = C_{A0}$$

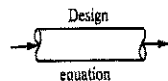
$$\text{when } X = X, C_A = C_A$$

Differentiating yields

$$\frac{dX}{dC_A} = \frac{-dC_A}{C_{A0}} \quad (2-25)$$

$$V = v_0 \int_{C_A}^{C_{A0}} \frac{dC_A}{-r_A}$$

$$\tau = \int_{C_A}^{C_{A0}} \frac{dC_A}{-r_A} \quad (2-26)$$



Valid only if $v = v_0$

Equation (2-26) is a form of the design equation for constant volumetric flow rate v_0 that may prove more useful in determining the space time or reactor volume for reaction rates that depend only on the concentration of one species.

Figure 2-11 shows a typical curve of the reciprocal reaction rate as a function of concentration for an isothermal reaction carried out at constant volume. For reaction orders greater than zero, the rate decreases as concentration decreases. The area under the curve gives the space time necessary to reduce the concentration of A from C_{A0} to C_{A1} .

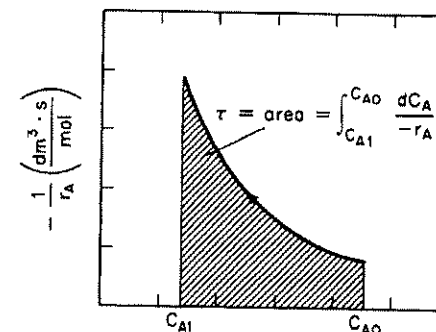


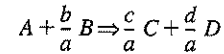
Figure 2-11 Determining the space time, τ .

To summarize these last examples, we have seen that in the design of reactors that are to be operated at conditions (e.g., temperature, initial concentration) identical to those at which the reaction rate data were obtained, detailed knowledge of the kinetic rate law $-r_A$ is not always necessary. In some instances it may be possible to scale up a laboratory-bench or pilot-plant reaction system solely from knowledge of $-r_A$ as a function of X or C_A . Unfortunately for most reactor systems, a scale-up process cannot be achieved simply from a knowledge of $-r_A$ as a function of X . In Chapter 3 we present elementary forms of the kinetic rate law from which the design equations can be evaluated, either by graphical or numerical integration or with the aid of a table of integrals.

SUMMARY

1. The points of this chapter are threefold:
 - a. To define the parameter *conversion* and to rewrite the mole balances in terms of conversion.
 - b. To show that by expressing $-r_A$ as a function of conversion, a number of reactors and reaction systems can be sized or a conversion be calculated from a given reactor size.
 - c. To relate the relative rates of reaction of reactants and products.

2. For the reaction



The relative rates of reaction can be written either as

$$\begin{aligned} \frac{-r_A}{a} &= \frac{-r_B}{b} = \frac{r_C}{c} = \frac{r_D}{d} \\ \text{or} \\ \frac{r_A}{-a} &= \frac{r_B}{-b} = \frac{r_C}{c} = \frac{r_D}{d} \end{aligned} \quad (\text{S2-1})$$

3. The conversion X is the moles of A reacted per mole of A fed.

For batch systems: $X = \frac{N_{A0} - N_A}{N_{A0}} \quad (\text{S2-2})$

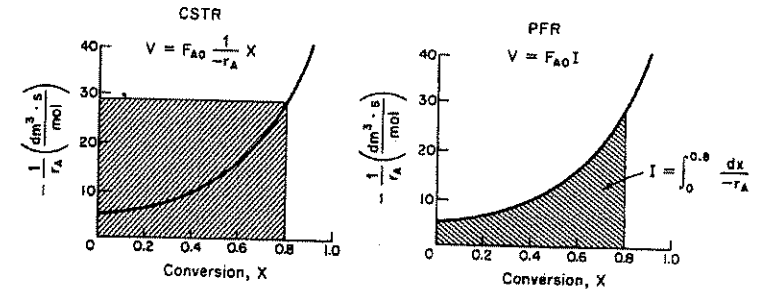
For flow systems: $X = \frac{F_{A0} - F_A}{F_{A0}} \quad (\text{S2-3})$

4. For reactors in series with no side streams or multiple feeds, the evaluation of the design equations may be simplified by letting the conversion represent the total moles reacted up to a particular point in the series of reactors.
5. In terms of the conversion, the differential and integral forms of the reactor design equations become:

	Differential Form	Algebraic Form	Integral Form
Batch	$N_{A0} \frac{dX}{dt} = -r_A V$		$t = N_{A0} \int_0^X \frac{dX}{-r_A V}$ and $\int_0^t V(t) dt = N_{A0} \int_0^X \frac{dX}{-r_A}$
CSTR		$V = \frac{F_{A0}(X_{\text{out}} - X_{\text{in}})}{(-r_A)_{\text{out}}}$	
PFR	$F_{A0} \frac{dX}{dV} = -r_A$		$V = F_{A0} \int_{X_{\text{in}}}^{X_{\text{out}}} \frac{dX}{-r_A}$
PBR	$F_{A0} \frac{dX}{dW} = -r'_A$		$W = F_{A0} \int_{X_{\text{in}}}^{X_{\text{out}}} \frac{dX}{-r'_A}$

6. If the rate of disappearance is given as a function of conversion, the following graphical techniques can be used to size a CSTR and a plug-flow reactor.

Levenspiel plots

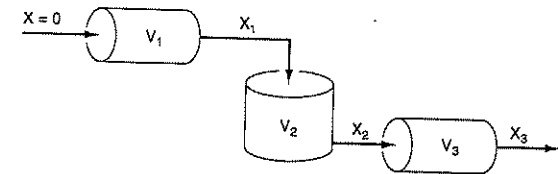


The PFR integral could also be evaluated by

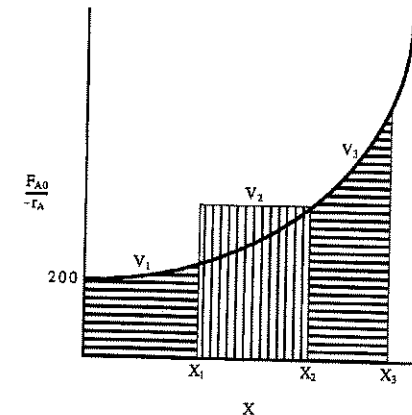
$$V = \int_0^{0.8} \frac{F_{A0}}{-r_A} dX \quad (\text{S2-4})$$

$$= \frac{0.2}{3} \left[\frac{F_{A0}}{-r_A(0)} + \frac{4F_{A0}}{-r_A(0.2)} + \frac{2F_{A0}}{-r_A(0.4)} + \frac{4F_{A0}}{-r_A(0.6)} + \frac{F_{A0}}{-r_A(0.8)} \right]$$

[see Equation (A-22) in Appendix A.4]. For the case of reactors in series, for which there are no side streams, the conversion is based on the total conversion up to a specified point. For the reaction sequence



the reactor volumes can be determined from the areas under the curve of a Levenspiel plot as shown below.



7. Space time, τ , and space velocity, SV, are given by

$$\tau = \frac{V}{v_0} \quad (\text{S2-5})$$

$$\text{SV} = \frac{v_0}{V} \quad (\text{S2-6})$$

In evaluating space velocity, the entering volumetric flow rate is usually referred to standard temperature and pressure.

8. Other definitions:

LHSV = liquid hourly space velocity, h^{-1}

GHSV = gas hourly space velocity, h^{-1} at STP.

QUESTIONS AND PROBLEMS

The subscript to each of the problem numbers indicates the level of difficulty: A, least difficult; D, most difficult.

A = ● B = ■ C = ◆ D = ◆◆

In each of the questions and problems below, rather than just drawing a box around your answer, write a sentence or two describing how you solved the problem, the assumptions you made, the reasonableness of your answer, what you learned, and any other facts you want to include. You may wish to refer to W. Strunk and E. B. White, *The Elements of Style* (New York: Macmillan, 1979) and Joseph M. Williams, *Style: Ten Lessons in Clarity & Grace* (Glenview, Ill.: Scott, Foresman 1989) to enhance the quality of your sentences.

- P2-1_A** Without referring back, make a list of the most important items you learned in this chapter. What do you believe was the overall purpose of the chapter?
- P2-2_A** What if:
- you needed to estimate the reactor volume necessary to achieve 98% conversion using the data in Table 2-1?
 - you were asked to use the data in Table 2-1 to calculate the CSTR reactor volume at a temperature 100°C higher than the temperature at which the data were taken?
- P2-3_A** Redo Example 2-7 for the cases when the intermediate conversions are (a) 30%, and (b) 70%. The molar flow rate is 52 mol/min.
- P2-4_A** The space time necessary to achieve 80% conversion in a CSTR is 5 h. Determine (if possible) the reactor volume required to process 2 ft³/min. What is the space velocity for this system?
- P2-5_A** There are two reactors of equal volume available for your use: one a CSTR, the other a PFR. The reaction is second order ($-r_A = kC_A^2 = kC_{A0}^2(1-X)^2$), irreversible, and is carried out isothermally.



There are three ways you can arrange your system:

- Reactors in series: CSTR followed by PFR
 - Reactors in series: PFR followed by CSTR
 - Reactors in parallel with half the feed rate going to each reactor after which the exit streams are mixed
- If possible, state which system will give the highest overall conversion.
 - If possible, state which system will give the lowest overall conversion.
 - If in one or more of the cases above it is not possible to obtain an answer, explain why. (*final exam, winter 1996*)
 - Comment on whether or not this is a reasonable final exam problem.

P2-6_B The exothermic reaction



was carried out adiabatically and the following data recorded:

X	0	0.2	0.4	0.5	0.6	0.8	0.9
$-r_A$ (mol/dm ³ ·min)	10	16.67	50	50	50	12.5	9.09

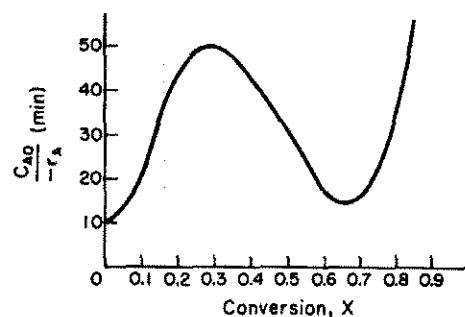
The entering molar flow rate of A was 300 mol/min.

- What are the PFR and CSTR volumes necessary to achieve 40% conversion? ($V_{\text{PFR}} = 7.2 \text{ dm}^3$, $V_{\text{CSTR}} = 2.4 \text{ dm}^3$)
- Over what range of conversions would the CSTR and PFR reactor volumes be identical?
- What is the maximum conversion that can be achieved in a 10.5-dm³ CSTR?
- What conversion can be achieved if a 7.2-dm³ PFR is followed in series by a 2.4-dm³ CSTR?
- What conversion can be achieved if a 2.4-dm³ CSTR is followed in a series by a 7.2-dm³ PFR?
- Plot the conversion and rate of reaction as a function of PFR reactor volume up to a volume of 10 dm³.

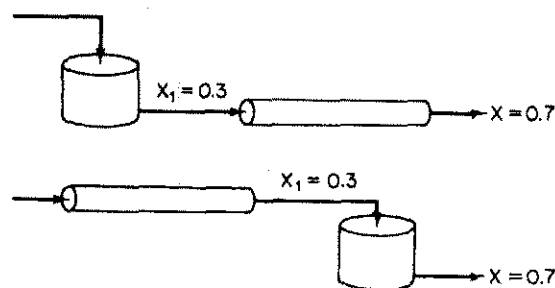
P2-7_C *Sgt. Nigel Ambercromby.* Worthless Chemical has been making tirene (B) from butalane (A) (both dark liquids) using a 8.0 ft³ CSTR followed by a 3.1 ft³ PFR. The entering flow rate is 1 ft³/min. A conversion of approximately 81% is achieved using this arrangement. The rate is shown as a function of conversion in Figure P2-8(a). The CSTR is identical to the one of the battery of CSTRs shown in Figure 1-11. There is a preheater upstream of the CSTR that heats the feed to 60°C. One morning the plant manager, Dr. Pakbed, arrived and found that the conversion had dropped to approximately 24%. After inspecting the reactors, the PFR was found to be working perfectly, but a dent was found in the CSTR that may have been caused by something like a fork lift truck. He also notes the CSTR, which normally makes a "woosh" sound is not as noisy as it was yesterday. The manager suspects foul play and calls in Sgt. Nigel Ambercromby from Scotland Yard. What are the first four questions Sgt. Ambercromby asks? Make a list of all the things that could cause the drop in conversion. Quantify the possible explanations with numerical calculations where possible. Dr. Pakbed tells Sgt. Ambercromby that he must achieve a conversion greater than 50% to meet production schedules downstream. Sgt. Ambercromby says, "I think I know how you could do this immediately." What does Ambercromby have in mind? [with Dan Dixon, ChE 344 W'97]



P2-8_B Figure P2-8a shows $C_{A0}/-r_A$ versus X_A for a nonisothermal, nonelementary, multiple-reaction liquid-phase decomposition of reactant A.



(a)



(b)

Figure P2-8

- Consider the two systems shown in Figure P2-8b in which a CSTR and plug-flow reactor are connected in series. The intermediate conversion is 0.3 and the final conversion is 0.7. How should the reactors be arranged to obtain the minimum total reactor volume? Explain.
- If the volumetric flow rate is 50 L/min, what is the minimum total reactor volume? (Ans. $V = 750 \text{ dm}^3$)
- Is there a better means (i.e., smallest total volume achieving 70% conversion other than either of the systems proposed above? (Ans.: 512 L)
- At what conversion(s) would the required reactor volume be identical for either a CSTR or a tubular PFR? (Ans.: $X = 0.45$, and $X = ?$)
- Using the information in Figure P2-8a together with the CSTR design equation, make a plot of τ versus X . If the reactor volume is 700 L and the volumetric flow rate 50 L/min, what are the possible outlet conversions (i.e., multiple steady states) for this reactor?

P2-9_B The irreversible gas-phase nonelementary reaction



is to be carried out isothermally in a constant-pressure batch reactor. The feed is at a temperature of 227°C, a pressure of 1013 kPa, and its composition is 33.3% A and 66.7% B. Laboratory data taken under identical conditions are as follows (note that at $X = 0$, $-r_A = 0.00001$):

$-r_A \text{ (mol/dm}^3 \cdot \text{s)} \times 10^3$	0.010	0.005	0.002	0.001
X	0.0	0.2	0.4	0.6

- Estimate the volume of a plug-flow reactor required to achieve 30% conversion of A for an entering volumetric flow rate of 2 m³/min.
- Estimate the volume of a CSTR required to take the effluent from the plug-flow reactor (PFR) above and achieve 50% total conversion (based on species A fed to the PFR).
- What is the total volume of the two reactors?
- What is the volume of a single plug-flow reactor necessary to achieve 60% conversion? 80% conversion?
- What is the volume of a single CSTR necessary to achieve 50% conversion?
- What is the volume of a second CSTR to raise the conversion from 50% to 60%?
- Plot the rate of reaction and conversion as a function of PFR volume.
- Give a critique of the answers to this problem.

P2-10_A Estimate the reactor volumes of the two CSTRs and the PFR shown in Figure 2-7.

P2-11_D Don't calculate anything. Just go home and relax.

P2-12_B The curve shown in Figure 2-1 is typical of a reaction carried out isothermally, while the curve shown in Figure P2-12 is typical of an exothermic reaction carried out adiabatically.

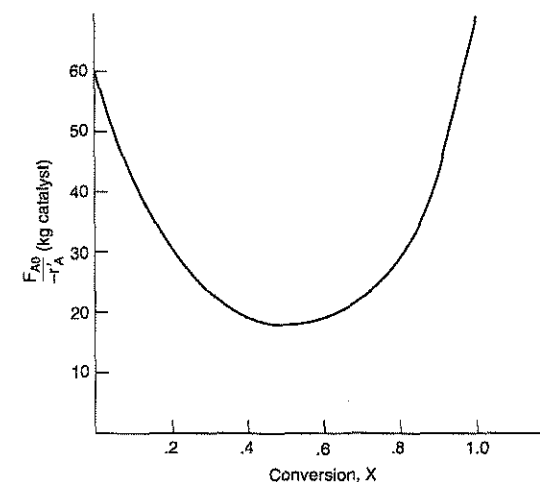


Figure P2-12 Exothermic reaction.

- Assuming that you have a CSTR and a PBR containing equal weights of catalyst, how should they be arranged for an isothermal reaction and for adiabatic reaction? In each case use the smallest amount of catalyst weight and still achieve 80% conversion.
- What is the catalyst weight necessary to achieve 80% conversion in a well-mixed reactor with catalyst particles (e.g., CSTR)?
- What "CSTR" weight is necessary to achieve 40% conversion?
- What PBR weight is necessary to achieve 80% conversion?
- What PBR weight is necessary to achieve 40% conversion?
- Plot the rate of reaction and conversion as a function of PBR volume.
- Write a paragraph describing how you would arrange reactors for different $-r_A'$ versus X curves.

Additional information: $F_{A0} = 2 \text{ mol/s}$.

P2-13 Using POLYMATH, MatLab, Mathematica, or some other software package, first fit the $-r_A$ versus X to a polynomial (i.e., $-r_A = a_0 + a_1X + a_2X^2$). Next use this polynomial and an ODE solver to plot the conversion down the length (i.e., volume) of a PFR and find the CSTR volume for 80% conversion for an entering molar flow rate of 5 mol/s.

- Use the data in Table 2-2.
- Use the data in Problem 2-6.
- Use the data in Problem 2-9.
- Use the data in Figure P2-12.

P2-14_D What is a typical reactor size for:¹

- cracking furnaces?
- packed beds?
- fluidized beds?
- pilot-plant-scale CSTR?
- industrial-scale CSTR?

For parts (b) and (c) specify the catalyst dimensions in addition to the dimensions of the reactor.

P2-15_B Review the reactor volumes calculated in each of the example problems in this chapter. Using the methanol reactor described in *Chem. Eng. Prog.*, 79(7), 64 (1983) as a basis of comparison, classify each of the reactor sizes and flow rates in the example problems as industrial, pilot plant, or laboratory scale.



CD-ROM MATERIAL

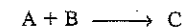
• Learning Resources

- Summary Notes for Lectures 1 and 2
- Web Module
 - Hippopotamus Digestive System
- Interactive Computer Modules
 - Reactor Staging
- Solved Problems
 - CDP2-A_B More CSTR and PFR Calculations - No Memorization
- FAQ [Frequently Asked Questions]- In Updates/FAQ icon section
- Additional Homework Problems

¹ See the Supplementary Reading lists for Chapters 1 and 2.



- CDP2-A** Use Levenspiel plots to calculate PFR and CSTR reactor volumes given $-r_A = f(X)$. (Includes Solution) [2nd Ed. P2-12_B]
- CDP2-B_A** An ethical dilemma as to how to determine the reactor size in a competitor's chemical plant. [2nd Ed. P2-18_B]
- CDP2-C_A** Use Levenspiel plots to calculate PFR and CSTR volumes.
- CDP2-D_A** Use Levenspiel plots to calculate CSTR and PFR volumes for the reaction



SUPPLEMENTARY READING

- Further discussion of stoichiometry may be found in

HIMMELBLAU, D. M., *Basic Principles and Calculations in Chemical Engineering*, 6th ed. Upper Saddle River, N.J.: Prentice Hall, 1996, Chap. 2.

FELDER, R. M., and R. W. ROUSSEAU, *Elementary Principles of Chemical Processes*, 2nd ed. New York: Wiley, 1986, Chap. 4.

- Further discussion of the proper staging of reactors in series for various rate laws, in which a plot of $-1/r_A$ versus X is given, is presented in

LEVENSPIEL, O., *Chemical Reaction Engineering*, 2nd ed. New York: Wiley, 1972, Chap. 6 (especially pp. 139–156).

HILL, C. G., *An Introduction to Chemical Engineering Kinetics and Reactor Design*. New York: Wiley, 1977, Chap. 8.

Rate Laws and Stoichiometry 3

Kinetics is nature's way of preventing everything from happening all at once.

—S. E. LeBlanc

We have shown that in order to calculate the time necessary to achieve a given conversion X in a batch system, or to calculate the reactor volume needed to achieve a conversion X in a flow system, we need to know the reaction rate as a function of conversion. In this chapter we show how this functional dependence is obtained. First there is a brief discussion of *chemical kinetics*, emphasizing definitions, which illustrates how the reaction rate depends on the concentrations of the reacting species. This discussion is followed by instructions on how to convert the reaction rate law from the concentration dependence to a dependence on conversion. Once this dependence is achieved, we can design a number of isothermal reaction systems.

3.1 Basic Definitions

A *homogeneous reaction* is one that involves only one phase. A *heterogeneous reaction* involves more than one phase, and reaction usually occurs at or very near the interface between the phases. An *irreversible reaction* is one that proceeds in only one direction and continues in that direction until the reactants are exhausted. A *reversible reaction*, on the other hand, can proceed in either direction, depending on the concentrations of reactants and products relative to the corresponding equilibrium concentrations. An irreversible reaction behaves as if no equilibrium condition exists. Strictly speaking, no chemical reaction is completely irreversible, but in very many reactions the equilibrium point lies so far to the right that they are treated as irreversible reactions.

Types of reactions

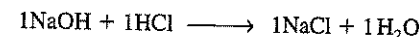
The rate law gives the relationship between reaction rate and concentration

3.1.1 The Reaction Rate Constant

In the chemical reactions considered in the following paragraphs, we take as the basis of calculation a species A , which is one of the reactants that is disappearing as a result of the reaction. The limiting reactant is usually chosen as our basis for calculation. The rate of disappearance of A , $-r_A$, depends on temperature and composition. For many reactions it can be written as the product of a *reaction rate constant* k and a function of the concentrations (activities) of the various species involved in the reaction:

$$-r_A = [k_A(T)] [f_n(C_A, C_B, \dots)] \quad (3-1)$$

The algebraic equation that relates $-r_A$ to the species concentrations is called the kinetic expression or **rate law**. The specific rate of reaction, k_A , like the reaction rate $-r_A$, is always referred to a particular species in the reactions and normally should be subscripted with respect to that species. However, for reactions in which the stoichiometric coefficient is 1 for all species involved in the reaction, for example,



we shall delete the subscript on the specific reaction rate:

$$k = k_{\text{NaOH}} = k_{\text{HCl}} = k_{\text{NaCl}} = k_{\text{H}_2\text{O}}$$

The reaction rate constant k is not truly a constant, but is merely independent of the concentrations of the species involved in the reaction. The quantity k is also referred to as the **specific reaction rate (constant)**. It is almost always strongly dependent on temperature. In gas-phase reactions, it depends on the catalyst and may be a function of total pressure. In liquid systems it can also be a function of total pressure, and in addition can depend on other parameters, such as ionic strength and choice of solvent. These other variables normally exhibit much less effect on the specific reaction rate than does temperature, so for the purposes of the material presented here it will be assumed that k_A depends only on temperature. This assumption is valid in most laboratory and industrial reactions and seems to work quite well.

It was the great Swedish chemist Arrhenius who first suggested that the temperature dependence of the specific reaction rate, k_A , could be correlated by an equation of the type

$$k_A(T) = A e^{-E/RT} \quad (3-2)$$

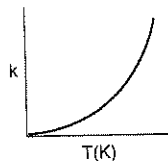
Arrhenius equation

where A = preexponential factor or frequency factor

E = activation energy, J/mol or cal/mol

R = gas constant = $8.314 \text{ J/mol} \cdot \text{K} = 1.987 \text{ cal/mol} \cdot \text{K}$

T = absolute temperature, K



Equation (3-2), known as the *Arrhenius equation*, has been verified empirically to give the temperature behavior of most reaction rate constants within experimental accuracy over fairly large temperature ranges.

The activation energy E has been equated with a minimum energy that must be possessed by reacting molecules before the reaction will occur. From the kinetic theory of gases, the factor $e^{-E/RT}$ gives the fraction of the collisions between molecules that together have this minimum energy E . Although this might be an acceptable elementary explanation, some suggest that E is nothing more than an empirical parameter correlating the specific reaction rate to temperature.¹ (See Appendix G) Other authors take exception to this interpretation; for example, Tolman's² interpretation of activation energy is that it is the difference between the *average energy of those molecules that do react* and the *average energy of all reactant molecules*. Nevertheless, postulation of the Arrhenius equation remains the greatest single step in chemical kinetics, and retains its usefulness today, nearly a century later.

The activation energy is determined experimentally by carrying out the reaction at several different temperatures. After taking the natural logarithm of Equation (3-2),

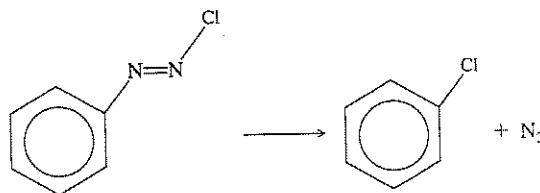
Calculation of the activation energy

$$\ln k_A = \ln A - \frac{E}{R} \left(\frac{1}{T} \right) \quad (3-3)$$

it can be seen that a plot of $\ln k_A$ versus $1/T$ should be a straight line whose slope is proportional to the activation energy.

Example 3-1 Determination of the Activation Energy

Calculate the activation energy for the decomposition of benzene diazonium chloride to give chlorobenzene and nitrogen:



using the following information for this first-order reaction:

k (s^{-1})	0.00043	0.00103	0.00180	0.00355	0.00717
T (K)	313.0	319.0	323.0	328.0	333.0

¹ M. Karplus, R. N. Porter, and R. D. Sharma, *J. Chem. Phys.*, 43, 3259 (1965); D. G. Truhlar, *J. Chem. Educ.*, 55(5), 310 (1978).

² R. C. Tolman, *Statistical Mechanics with Applications to Physics and Chemistry* (New York: Chemical Catalog Company, 1927), pp. 260–270.

Solution

By converting Equation (3-3) to log base 10,

$$\log k = \log A - \frac{E}{2.3R} \left(\frac{1}{T} \right) \quad (E3-1.1)$$

we can use semilog paper to determine E quite readily by first forming the following table from the data above:

k (s^{-1})	0.00043	0.00103	0.00180	0.00355	0.00717
$1000/T$ (K^{-1})	3.20	3.14	3.10	3.05	3.0

Then we plot the data directly on semilog paper as shown in Figure E3-1.1.

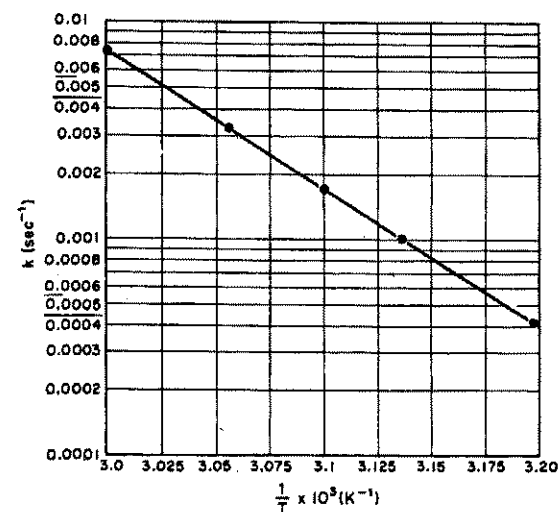


Figure E3-1.1

Although the slope can be determined by a number of methods as described in Appendix D, the decade method is chosen here. For two different points on Figure E3-1.1, we have

$$\log k_1 = \log A - \frac{E}{2.3R} \left(\frac{1}{T_1} \right)$$

$$\log k_2 = \log A - \frac{E}{2.3R} \left(\frac{1}{T_2} \right)$$

Subtracting yields

$$\log \frac{k_2}{k_1} = \frac{-E}{2.3R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (\text{E3-1.2})$$

$$E = - \frac{(2.3)(R) \log(k_2/k_1)}{1/T_2 - 1/T_1}$$

To use the decade method, choose $1/T_1$ and $1/T_2$ so that $k_2 = 0.1k_1$. Then, $\log(k_1/k_2) = 1$.

$$\text{When } k_1 = 0.005: \quad \frac{1}{T_1} = 0.00303$$

$$\text{When } k_2 = 0.0005: \quad \frac{1}{T_2} = 0.00319$$

Therefore,

$$\begin{aligned} E &= \frac{2.303R}{1/T_2 - 1/T_1} = \frac{(2.303)(8.314 \text{ J/mol} \cdot \text{K})}{(0.00319 - 0.00303)/\text{K}} \\ &= 120 \frac{\text{kJ}}{\text{mol}} \text{ or } 28.7 \text{ kcal/mol} \end{aligned}$$

The rate does not always double for a temperature increase of 10°C

There is a rule of thumb that states that the rate of reaction doubles for every 10°C increase in temperature. However, this is true only for a specific combination of activation energy and temperature. For example, if the activation energy is 53.6 kJ/mol , the rate will double only if the temperature is raised from 300 K to 310 K . If the activation energy is 147 kJ/mol , the rule will be valid only if the temperature is raised from 500 K to 510 K . (See Problem P3-5 for the derivation of this relationship.)

The larger the activation energy, the more temperature-sensitive is the rate of reaction. While there are no typical values of the frequency factor and activation energy for a first-order gas-phase reaction, if one were forced to make a guess, values of A and E might be 10^{13} s^{-1} and 300 kJ/mol . However, for families of reactions (e.g., halogenation), a number of correlations can be used to estimate the activation energy. One such correlation is the Polanyi-Semenov equation, which relates activation energy to the heat of reaction (see Problem P3-20). Another correlation relates activation energy to differences in bond strengths between products and reactants.³ While activation energy cannot be currently predicted a priori, significant research efforts are under way to calculate activation energies from first principles.⁴ (Also see Appendix J)

³ M. Boudart, *Kinetics of Chemical Processes* (Upper Saddle River, N.J.: Prentice Hall, 1968), p. 168. J. W. Moore and R. G. Pearson, *Kinetics and Mechanisms*, 3rd ed. (New York: Wiley, 1981), p. 199. S. W. Benson, *Thermochemical Kinetics*, 2nd ed. (New York: Wiley, 1976).

⁴ S. M. Senkan, *Detailed Chemical Kinetic Modeling: Chemical Reaction Engineering of the Future*, Advances in Chemical Engineering, Vol. 18 (San Diego: Academic Press, 1992), pp. 95-96.

Other expressions similar to the Arrhenius equation exist. One such expression is the temperature dependence derived from transition-state theory, which takes a form similar to Equation (3-2):

$$k(T) = A' T^n e^{-E'/RT} \quad (3-4)$$

in which $0 \leq n \leq 1$.

If Equations (3-2) and (3-4) are used to describe the temperature dependence for the same reaction data, it will be found that the activation energies E and E' will differ slightly.

3.1.2 The Reaction Order and Rate Law

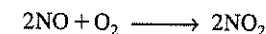
The dependence of the reaction rate $-r_A$ on the concentrations of the species present, $\text{fn}(C_j)$, is almost without exception determined by experimental observation. Although the functional dependence may be postulated from theory, experiments are necessary to confirm the proposed form. One of the most common general forms of this dependence is the product of concentrations of the individual reacting species, each of which is raised to a power, for example,

$$-r_A = k_A C_A^\alpha C_B^\beta \quad (3-5)$$

The exponents of the concentrations in Equation (3-5) lead to the concept of *reaction order*. The **order of a reaction** refers to the powers to which the concentrations are raised in the kinetic rate law.[†] In Equation (3-5), the reaction is α order with respect to reactant A, and β order with respect to reactant B. The overall order of the reaction, n , is

$$n = \alpha + \beta$$

For example, in the gas-phase reaction



Overall reaction order

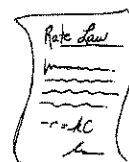
Strictly Speaking

[†] Strictly speaking, the reaction rates should be written in terms of the activities, a_i ($a_i = \gamma_i C_i$, where γ_i is the activity coefficient):

$$-r_A = k'_A a_A^\alpha a_B^\beta$$

However, for many reacting systems, the activity coefficients, γ_i , do not change appreciably during the course of the reaction and they are adsorbed in the specific reaction rate:

$$-r_A = k'_A a_A^\alpha a_B^\beta = k'_A (\gamma_A C_A)^\alpha (\gamma_B C_B)^\beta = (k'_A \gamma_A^\alpha \gamma_B^\beta) C_A^\alpha C_B^\beta = k_A C_A^\alpha C_B^\beta$$



the kinetic *rate law* is

$$-r_{\text{NO}} = k_{\text{NO}} C_{\text{NO}}^2 C_{\text{O}_2}$$

This reaction is second-order with respect to nitric oxide, first-order with respect to oxygen, and overall is a third-order reaction. In general, first- and second-order reactions are more commonly observed than zero- and third-order reactions.

The overall order of a reaction does not have to be an integer, nor does the order have to be an integer with respect to any individual component. As an example, consider the gas-phase synthesis of phosgene:

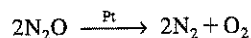


in which the kinetic *rate law* is

$$-r_{\text{CO}} = k C_{\text{CO}} C_{\text{Cl}_2}^{3/2}$$

This reaction is first-order with respect to carbon monoxide, three-halves order with respect to chlorine, and five-halves order overall.

Sometimes reactions have complex rate expressions that cannot be separated into solely temperature-dependent and concentration-dependent portions. In the decomposition of nitrous oxide over platinum,

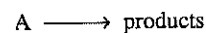


the kinetic *rate law* is

$$-r_{\text{N}_2\text{O}} = \frac{k_{\text{N}_2\text{O}} C_{\text{N}_2\text{O}}}{1 + k' C_{\text{O}_2}}$$

Both $k_{\text{N}_2\text{O}}$ and k' are strongly temperature-dependent. When a rate expression such as the one described above occurs, we can speak of reaction orders only under certain limiting conditions. For example, at very low concentrations of oxygen, the second term in the denominator would be negligible ($1 \gg k' C_{\text{O}_2}$) and the reaction would be "apparent" first-order with respect to nitrous oxide and first-order overall. However, if the concentration of oxygen were large enough so that the number 1 in the denominator were insignificant in comparison with the second term, $k' C_{\text{O}_2}$ ($k' C_{\text{O}_2} \gg 1$), the *apparent* reaction order would be -1 with respect to oxygen and 1 with respect to nitrous oxide. Rate expressions of this type are very common for liquid and gaseous reactions promoted by solid catalysts (see Chapter 10). They also occur occasionally in homogeneous reaction systems (see Chapter 7).

The units of the specific reaction rate, k_A , vary with the order of the reaction. Consider a reaction involving only one reactant, such as



Apparent reaction orders

Where do you find rate laws?

Very important references, but you should also look in the other literature before going to the lab

For this type of reaction, the rate laws corresponding to a zero-, first-, second-, third-order reaction, together with typical units for the corresponding rate constants, are:

$$\begin{aligned} \text{Zero-order:} \quad -r_A &= k_A: & (3-6) \\ \{k\} &= \text{mol}/(\text{dm}^3) \cdot \text{s} \end{aligned}$$

$$\begin{aligned} \text{First-order:} \quad -r_A &= k_A C_A: & (3-7) \\ \{k\} &= \text{s}^{-1} \end{aligned}$$

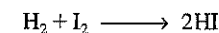
$$\begin{aligned} \text{Second-order:} \quad -r_A &= k_A C_A^2: & (3-8) \\ \{k\} &= (\text{dm}^3)/\text{mol} \cdot \text{s} \end{aligned}$$

$$\begin{aligned} \text{Third-order:} \quad -r_A &= k_A C_A^3: & (3-9) \\ \{k\} &= (\text{dm}^3/\text{mol})^2 \cdot \text{s}^{-1} \end{aligned}$$

The activation energy, frequency factor, and reaction orders for a large number of gas- and liquid-phase reactions can be found in the National Bureau of Standards' circulars and supplements.⁵ Also consult the journals listed at the end of Chapter 1.

3.1.3 Elementary Rate Laws and Molecularity

A reaction has an *elementary rate law* if the reaction order of each species is identical with the stoichiometric coefficient of that species for the reaction as written. For example, the oxidation of nitric oxide presented above has an elementary rate law under this definition, while the phosgene synthesis reaction does not. Another example of this type of reaction with an elementary rate law is the gas-phase reaction between hydrogen and iodine to form hydrogen iodide:



for which the rate law is

$$-r_{\text{H}_2} = k C_{\text{H}_2} C_{\text{I}_2}$$

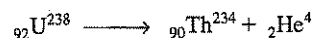
In some circles when a reaction has an elementary rate law it is referred to as an *elementary reaction*. A more restrictive definition of an elementary

⁵ *Tables of Chemical Kinetics: Homogeneous Reactions*, National Bureau of Standards Circular 510 (Sept. 28, 1951); Suppl. 1 (Nov. 14, 1956); Suppl. 2 (Aug. 5, 1960); Suppl. 3 (Sept. 15, 1961) (Washington, D.C.: U.S. Government Printing Office). *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling*, Evaluation No. 10, JPL Publication 92-20, Aug. 15, 1992, Jet Propulsion Laboratories, Pasadena, Calif.

reaction is sometimes encountered, and it involves the mechanism or molecular path of the reaction. This definition is discussed in Chapter 7.[†]

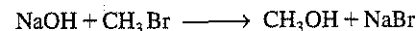
In the study of reaction orders and kinetic mechanisms, reference is sometimes made to the *molecularity* of a reaction. The molecularity is the number of atoms, ions, or molecules involved (colliding) in the rate-limiting step of the reaction. The terms *unimolecular*, *bimolecular*, and *termolecular* refer to reactions involving, respectively, one, two, or three atoms (or molecules) interacting or colliding in any one reaction step.

The most common example of a unimolecular reaction is radioactive decay, such as the spontaneous emission of an alpha particle from uranium 238 to give thorium and helium:



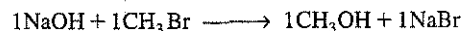
If the hydrogen-iodine and the nitric oxide oxidation reactions did indeed result simply from the collision of the molecular species named in the overall stoichiometric equations, they would be bimolecular and termolecular reactions, respectively. There is considerable doubt, though, about whether this actually occurs.

The reaction between methyl bromide and sodium hydroxide is classified as a nucleophilic aliphatic substitution:⁶



This irreversible reaction has an elementary rate law and is carried out in aqueous ethanol. Therefore, like almost all liquid-phase reactions, the density remains almost constant throughout the reaction. It is a general principle that for most liquid-phase reactions, the volume V for a batch reaction system and the volumetric flow rate v for a continuous-flow system will not change appreciably during the course of a chemical reaction.

We want to write the rate of disappearance of methyl bromide, $-r_{\text{MB}}$, in terms of the appropriate concentrations. Because this reaction is elementary the reaction orders agree with the stoichiometric coefficients.



$\alpha = 1$, first-order with respect to sodium hydroxide

$\beta = 1$, first-order with respect to methyl bromide (MB)

$$-r_{\text{MB}} = kC_{\text{NaOH}}C_{\text{CH}_3\text{Br}}$$

Overall, this reaction is second-order.

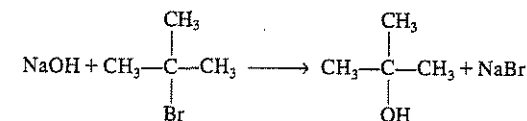
Strictly Speaking

[†] Strictly speaking, elementary reactions involve only single steps such as one iodide molecule colliding and reacting with one hydrogen molecule. However, most reactions involve multiple steps and pathways. For many of these reactions, the powers in the rate laws surprisingly agree with the stoichiometric coefficients. Consequently, to facilitate describing this class of reactions, reactions where the rate law powers and stoichiometric coefficients are identical may also be referred to as elementary reactions.

⁶ R. T. Morrison and R. N. Boyd, *Organic Chemistry*, 4th ed. (Needham Heights, Mass.: Allyn and Bacon, 1983).

Example 3-2 Describing a Reaction

Another nucleophilic aliphatic substitution is the reaction between sodium hydroxide and *tert*-butyl bromide (TBB):



State the reaction order with respect to each species as well as the overall reaction order and generally describe this reaction.

Solution

Just because this reaction is similar to the previous nucleophilic aliphatic substitution, one should not jump to the conclusion that the rate law and kinetics will be similar. *The rate law is determined from experimental observation. It relates the rate of reaction at a particular point to the species concentrations at that same point.* In this case if one consults an organic chemistry text,⁷ one will find that the rate law is

$$-r_{\text{TBB}} = kC_{\text{TBB}} \quad (\text{E3-2.1})$$

Using the definitions above, the reaction of sodium hydroxide with *tert*-butyl bromide (TBB) can be described as an irreversible, homogeneous, liquid-phase reaction which is first-order with respect to *tert*-butyl bromide, zero-order with respect to sodium hydroxide, overall first-order, and nonelementary.

3.1.4 Reversible Reactions

All rate laws for reversible reactions *must* reduce to the thermodynamic relationship relating the reacting species concentrations at equilibrium. At equilibrium, the rate of reaction is identically zero for all species (i.e., $-r_A \equiv 0$). That is, for the general reaction



the concentrations at equilibrium are related by the thermodynamic relationship (see Appendix C).

$$K_C = \frac{C_C^c C_D^d}{C_A^a C_B^b} \quad (3-10)$$

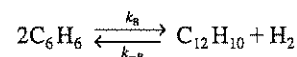
The units of K_C are $(\text{mol}/\text{dm}^3)^{d+c-b-a}$.

To illustrate how to write rate laws for reversible reactions we will use the combination of two benzene molecules to form one molecule of hydrogen

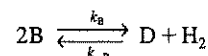
Thermodynamic
Equilibrium
Relationship

⁷ Ibid.

and one of diphenyl. In this discussion we shall consider this gas-phase reaction to be elementary and reversible:



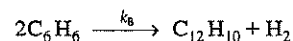
or symbolically,



The specific reaction rate, k_i , must be defined w.r.t. a particular species

The forward and reverse specific reaction rate constants, k_B and k_{-B} , respectively, will be defined with respect to benzene.

Benzene (B) is being depleted by the forward reaction



in which the rate of disappearance of benzene is

$$-r_{B,\text{forward}} = k_B C_B^2$$

If we multiply both sides of this equation by -1 , we obtain the expression for the rate of formation of benzene for the forward reaction:

$$r_{B,\text{forward}} = -k_B C_B^2 \quad (3-11)$$

For the reverse reaction between diphenyl (D) and hydrogen (H_2),



the rate of formation of benzene is given as

$$r_{B,\text{reverse}} = k_{-B} C_D C_{\text{H}_2} \quad (3-12)$$

The net rate of formation of benzene is the sum of the rates of formation from the forward reaction [i.e., Equation (3-11)] and the reverse reaction [i.e., Equation (3-12)]:

$$r_B \equiv r_{B,\text{net}} = r_{B,\text{forward}} + r_{B,\text{reverse}}$$

$$r_B = -k_B C_B^2 + k_{-B} C_D C_{\text{H}_2} \quad (3-13)$$

Multiplying both sides of Equation (3-13) by -1 , we obtain the rate law for the rate of disappearance of benzene, $-r_B$:

$$-r_B = k_B C_B^2 - k_{-B} C_D C_{\text{H}_2} = k_B \left(C_B^2 - \frac{k_{-B}}{k_B} C_D C_{\text{H}_2} \right)$$

$$-r_B = k_B \left(C_B^2 - \frac{C_D C_{\text{H}_2}}{K_C} \right) \quad (3-14)$$

Elementary reversible
A \rightleftharpoons B

$$-r_A = k \left(C_A - \frac{C_B}{K_c} \right)$$

where

$$\frac{k_B}{k_{-B}} = K_C = \text{concentration equilibrium constant}$$

The equilibrium constant decreases with increasing temperature for exothermic reactions and increases with increasing temperature for endothermic reactions.

We need to check to see if the rate law given by Equation (3-14) is thermodynamically consistent at equilibrium. Using Equation (3-10) and substituting the appropriate species concentration and exponents, thermodynamics tells us that

$$K_C = \frac{C_{\text{De}} C_{\text{H}_2\text{e}}}{C_{\text{Be}}^2} \quad (3-15)$$

At equilibrium, $-r_B \equiv 0$, and the rate law given by Equation (3-14) becomes

$$-r_B \equiv 0 = k_B \left[C_{\text{Be}}^2 - \frac{C_{\text{De}} C_{\text{H}_2\text{e}}}{K_C} \right]$$

Rearranging, we obtain

$$K_C = \frac{C_{\text{De}} C_{\text{H}_2\text{e}}}{C_{\text{Be}}^2}$$

which is identical to Equation (3-15).

A further discussion of the equilibrium constant and its thermodynamic relationship is given in **Appendix C**.

Finally, we want to rewrite the rate of formation of diphenyl and hydrogen in terms of concentration. The rate of formation of these species must have the same functional dependence on concentrations as does the rate of disappearance of benzene. The rate of formation of diphenyl is

$$r_D = k_D \left[C_B^2 - \frac{C_D C_{\text{H}_2}}{K_C} \right] \quad (3-16)$$

Using the relationship given by Equation (2-20) for the general reaction

$$\frac{r_A}{-a} = \frac{r_B}{-b} = \frac{r_C}{c} = \frac{r_D}{d} \quad (2-20)$$

we can obtain the relationship between the various specific reaction rates, k_B , k_D :

$$\frac{r_D}{1} = \frac{r_B}{-2} = \frac{k_B}{2} \left[C_B^2 - \frac{C_D C_{\text{H}_2}}{K_C} \right] \quad (3-17)$$

At equilibrium the rate law must reduce to an equation consistent with thermodynamic equilibrium

Comparing Equations (3-16) and (3-17), we see the relationship between the specific reaction rate with respect to diphenyl and the specific reaction rate with respect to benzene is

$$k_D = \frac{k_B}{2}$$

Example 3-3 Formulating a Reversible Rate Law

The exothermic reaction



is virtually irreversible at low temperatures and the rate law is

$$-r_A = k_A C_A^{1/2} C_B \quad (\text{E3-3.2})$$

Suggest a rate law that is valid at high temperatures, where the reaction is reversible:



Solution

The rate law for the reversible reaction *must*

1. satisfy thermodynamic relationships at equilibrium, and
2. reduce to the irreversible rate law when the concentration of one or more of the reaction products is zero.

We know from thermodynamics that the equilibrium relationship for Reaction (E3-3.1) as written is

$$K_C = \frac{C_D^2}{C_A C_B^2} \quad \text{with units} \quad [K_C] = \frac{\text{dm}^3}{\text{mol}} \quad (\text{E3-3.4})$$

Rearranging Equation (E3-3.4) in the form

$$C_A C_B^2 - \frac{C_D^2}{K_C} = 0$$

suggests that we try a reversible rate law of the form

$$-r_A = k_A \left[C_A C_B^2 - \frac{C_D^2}{K_C} \right] \quad (\text{E3-3.5})$$

Equation (E3-3.5) satisfies the equilibrium conditions but does not simplify to the initial, irreversible rate when $C_D = 0$. Substituting $C_D = 0$ into the equation being tested yields

These criteria must be satisfied

$$-r_{A0} = k_A C_{A0} C_{B0}^2 \quad (\text{E3-3.6})$$

Equation (E3-3.6) does not agree with Equation (E3-3.2) and therefore the rate law given by Equation (E3-3.5) is not valid.

The one-half power in the rate law suggests that we might take the square root of Equation (E3-3.4):

$$\sqrt{K_C} = \frac{C_D}{C_A^{1/2} C_B} = K_{C2} \quad [K_{C2}] \text{ is in units of } \left(\frac{\text{dm}^3}{\text{mol}} \right)^{1/2} \quad (\text{E3-3.7})$$

Rearranging gives

$$C_A^{1/2} C_B - \frac{C_D}{K_{C2}} = 0 \quad (\text{E3-3.8})$$

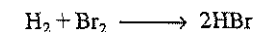
Using this new equilibrium constant, K_{C2} , we can formulate another suggestion for the reaction rate expression:

$$-r_A = k_A \left[C_A^{1/2} C_B - \frac{C_D}{K_{C2}} \right] \quad (\text{E3-3.9})$$

Note that this expression satisfies both the thermodynamic relationship (see the definition of K_{C2}) and reduces to the irreversible rate law when $C_D = 0$. The form of the irreversible rate law provides a big clue as to the form of the reversible reaction rate expression.

3.1.5 Nonelementary Rate Laws and Reactions

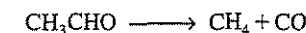
It is interesting to note that although the reaction orders correspond to the stoichiometric coefficients for the reaction between hydrogen and iodine, the rate expression for the reaction between hydrogen and another halogen, bromine, is quite complex. This nonelementary reaction



proceeds by a free-radical mechanism, and its reaction rate law is

$$r_{\text{HBr}} = \frac{k_1 C_{\text{H}_2} C_{\text{Br}_2}^{1/2}}{k_2 + C_{\text{HBr}}/C_{\text{Br}_2}} \quad (\text{3-18})$$

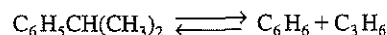
Another reaction involving free radicals is the vapor-phase decomposition of acetaldehyde:



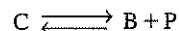
At a temperature of about 500°C, the order of the reaction is three-halves with respect to acetaldehyde.

$$-r_{\text{CH}_3\text{CHO}} = kC_{\text{CH}_3\text{CHO}}^{3/2} \quad (3-19)$$

In many gas-solid catalyzed reactions it is sometimes preferable to write the rate law in terms of partial pressures rather than concentrations. One such example is the reversible catalytic decomposition of cumene, C, to form benzene, B, and propylene, P:



The reaction can be written symbolically as



It was found experimentally that the reaction follows Langmuir-Hinshelwood kinetics and the rate law is (see Chapter 10)

$$-r'_C = \frac{k(P_C - P_B P_P / K_P)}{1 + K_C P_C + K_B P_B} \quad (3-20)$$

where K_P is the pressure equilibrium constant with units of atm (or kPa); K_C and K_B are the adsorption constants with units of atm^{-1} (or kPa^{-1}); and the specific reaction rate, k , has units of

$$[k] = \frac{\text{mol cumene}}{\text{kg cat} \cdot \text{s} \cdot \text{atm}}$$

We see that at equilibrium ($-r'_C = 0$) the rate law for the reversible reaction is indeed thermodynamically consistent:

$$-r'_C = 0 = k \frac{P_{C_e} - P_{B_e} P_{P_e} / K_P}{1 + K_C P_{C_e} + K_B P_{B_e}}$$

Solving for K_P yields

$$K_P = \frac{P_{B_e} P_{P_e}}{P_{C_e}}$$

which is identical to the expression obtained from thermodynamics.

To express the rate of decomposition of cumene $-r'_C$ as a function of conversion, replace the partial pressure with concentration, using the ideal gas law:

$$P_C = C_C RT \quad (3-21)$$

and then express concentration in terms of conversion.

The rate of reaction per unit weight of catalyst, $-r'_A$, and the rate of reaction per unit volume, $-r_A$, are related through the bulk density ρ_b of the catalyst particles in the fluid media:

$$-r_A = \rho_b (-r'_A) \quad (3-22)$$

$$\frac{\text{moles}}{\text{time} \cdot \text{volume}} = \left(\frac{\text{mass}}{\text{volume}} \right) \left(\frac{\text{moles}}{\text{time} \cdot \text{mass}} \right)$$

In fluidized catalytic beds the bulk density is normally a function of the flow rate through the bed.

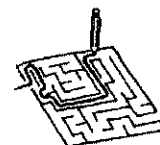
3.2 Present Status of Our Approach to Reactor Sizing and Design

In Chapter 2 we showed how it was possible to size CSTRs, PFRs, and PBRs using the design equations in Table 3-1 if the rate of disappearance of A is known as a function of conversion, X :

$$-r_A = g(X)$$

TABLE 3-1. DESIGN EQUATIONS

	Differential Form	Algebraic Form	Integral Form
Batch	$N_{A0} \frac{dX}{dt} = -r_A V \quad (2-6)$		$t = N_{A0} \int_0^X \frac{dX}{-r_A V} \quad (2-9)$
Backmix (CSTR)		$V = \frac{F_{A0} X}{-r_A} \quad (2-13)$	
Tubular (PFR)	$F_{A0} \frac{dX}{dV} = -r_A \quad (2-15)$		$V = F_{A0} \int_0^X \frac{dX}{-r_A} \quad (2-16)$
Packed bed (PBR)	$F_{A0} \frac{dX}{dW} = -r'_A \quad (2-17)$		$W = F_{A0} \int_0^X \frac{dX}{-r'_A} \quad (2-18)$



The design equations

In general, information in the form $-r_A = g(X)$ is not available. However, we have seen in Section 3.1 that the rate of disappearance of A, $-r_A$, is normally expressed in terms of the concentration of the reacting species. This functionality,

$$-r_A = k[\text{fn}(C_A, C_B, \dots)] \quad (3-1)$$

is called a *rate law*. In Section 3.3 we show how the concentration of the reacting species may be written in terms of the conversion X ,

$$C_j = h_j(X)$$

With these additional relationships, one observes that if the rate law is given and the concentrations can be expressed as a function of conversion, *then in fact we have $-r_A$ as a function of X and this is all that is needed to evaluate the design equations*. One can use either the numerical techniques described in Chapter 2, or, as we shall see in Chapter 4, a table of integrals.

$$\begin{aligned} -r_A &= f(C_j) \\ &+ \\ C_j &= h_j(X) \\ &\downarrow \\ -r_A &= g(X) \\ &\text{and then we can} \\ &\text{design isothermal} \\ &\text{reactors} \end{aligned}$$

3.3 Stoichiometric Table

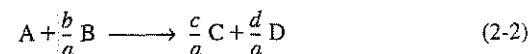
Now that we have shown how the rate law can be expressed as a function of concentrations, we need only express concentration as a function of conversion in order to carry out calculations similar to those presented in Chapter 2 to size reactors. If the rate law depends on more than one species, we must relate the concentrations of the different species to each other. This relationship is most easily established with the aid of a stoichiometric table. This table presents the stoichiometric relationships between reacting molecules for a single reaction. That is, it tells us how many molecules of one species will be formed during a chemical reaction when a given number of molecules of another species disappears. These relationships will be developed for the general reaction



Recall that we have already used stoichiometry to relate the relative rates of reaction for Equation (2-1):

$$\frac{r_A}{-a} = \frac{r_B}{-b} = \frac{r_C}{c} = \frac{r_D}{d} \quad (2-20)$$

In formulating our stoichiometric table we shall take species A as our basis of calculation (i.e., limiting reactant) and then divide through by the stoichiometric coefficient of A,



in order to put everything on a basis of "per mole of A."

Next, we develop the stoichiometric relationships for reacting species that give the change in the number of moles of each species (i.e., A, B, C, and D).

3.3.1 Batch Systems

Figure 3-1 shows a batch system in which we will carry out the reaction given by Equation (2-2). At time $t = 0$ we will open the reactor and place a number of moles of species A, B, C, D, and I (N_{A0} , N_{B0} , N_{C0} , N_{D0} , and N_I , respectively) into the reactor.

Species A is our basis of calculation and N_{A0} is the number of moles of A initially present in the reactor. Of these, $N_{A0}X$ moles of A are consumed in the system as a result of the chemical reaction, leaving ($N_{A0} - N_{A0}X$) moles of A in the system. That is, the number of moles of A remaining in the reactor after conversion X has been achieved is

$$N_A = N_{A0} - N_{A0}X = N_{A0}(1 - X)$$

The complete stoichiometric table for the reaction shown in Equation (2-2) taking place in a batch reactor is presented in Table 3-2.

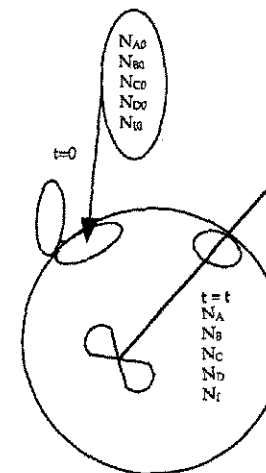


Figure 3-1 Batch reactor.

To determine the number of moles of each species remaining after $N_{A0}X$ moles of A have reacted, we form the stoichiometric table (Table 3-2). This stoichiometric table presents the following information:

Column 1: the particular species

Column 2: the number of moles of each species initially present

Column 3: the change in the number of moles brought about by reaction

Column 4: the number of moles remaining in the system at time t

Components of the
stoichiometric
table

TABLE 3-2. STOICHIOMETRIC TABLE FOR A BATCH SYSTEM

Species	Initially (mol)	Change (mol)	Remaining (mol)
A	N_{A0}	$-(N_{A0}X)$	$N_A = N_{A0} - N_{A0}X$
B	N_{B0}	$-\frac{b}{a}(N_{A0}X)$	$N_B = N_{B0} - \frac{b}{a}N_{A0}X$
C	N_{C0}	$\frac{c}{a}(N_{A0}X)$	$N_C = N_{C0} + \frac{c}{a}N_{A0}X$
D	N_{D0}	$\frac{d}{a}(N_{A0}X)$	$N_D = N_{D0} + \frac{d}{a}N_{A0}X$
I (inerts)	N_{I0}	—	$N_I = N_{I0}$
Totals	N_{T0}		$N_T = N_{T0} + \left(\frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1\right)N_{A0}X$

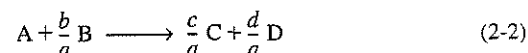
To calculate the number of moles of species B remaining at time t we recall that at time t the number of moles of A that have reacted is $N_{A0}X$. For every mole of A that reacts, b/a moles of B must react; therefore, the total number of moles of B that have reacted is

$$\begin{aligned}\text{moles B reacted} &= \frac{\text{moles B reacted}}{\text{moles A reacted}} \cdot \text{moles A reacted} \\ &= \frac{b}{a} (N_{A0}X)\end{aligned}$$

Because B is disappearing from the system, the sign of the "change" is negative. N_{B0} is the number of moles initially in the system. Therefore, the number of moles of B remaining in the system, N_B , is given in the last column of Table 3-2 as

$$N_B = N_{B0} - \frac{b}{a} N_{A0}X$$

The complete stoichiometric table delineated in Table 3-2 is for all species in the reaction



The stoichiometric coefficients in parentheses ($d/a + c/a - b/a - 1$) represent the increase in the total number of moles per mole of A reacted. Because this term occurs often in our calculations it is given the symbol δ :

$$\delta = \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1 \quad (3-23)$$

The total number of moles can now be calculated from the equation

$$N_T = N_{T0} + \delta N_{A0}X$$

We recall from Chapter 1 that the kinetic rate law (e.g., $-r_A = kC_A^2$) is a function solely of the intensive properties of the reacting materials (e.g., temperature, pressure, concentration, and catalysts, if any). The reaction rate, $-r_A$, usually depends on the concentration of the reacting species raised to some power. Consequently, to determine the reaction rate as a function of conversion X , we need to know the concentrations of the reacting species as a function of conversion.

The concentration of A is the number of moles of A per unit volume:

$$C_A = \frac{N_A}{V}$$

After writing similar equations for B, C, and D, we use the stoichiometric table to express the concentration of each component in terms of the conversion X :

$$\begin{aligned}C_A &= \frac{N_A}{V} = \frac{N_{A0}(1-X)}{V} \\ C_B &= \frac{N_B}{V} = \frac{N_{B0} - (b/a)N_{A0}X}{V} \\ C_C &= \frac{N_C}{V} = \frac{N_{C0} + (c/a)N_{A0}X}{V} \\ C_D &= \frac{N_D}{V} = \frac{N_{D0} + (d/a)N_{A0}X}{V}\end{aligned} \quad (3-24)$$

We further simplify these equations by defining the parameter Θ_i , which allows us to factor N_{A0} in each of the expressions for concentration:

$$\begin{aligned}\Theta_i &= \frac{N_{i0}}{N_{A0}} = \frac{C_{i0}}{C_{A0}} = \frac{y_{i0}}{y_{A0}} \\ C_B &= \frac{N_{A0}[N_{B0}/N_{A0} - (b/a)X]}{V} = \frac{N_{A0}[\Theta_B - (b/a)X]}{V} \quad \Theta_B = \frac{N_{B0}}{N_{A0}} \\ C_C &= \frac{N_{A0}[\Theta_C + (c/a)X]}{V} \\ C_D &= \frac{N_{A0}[\Theta_D + (d/a)X]}{V}\end{aligned} \quad (3-25)$$

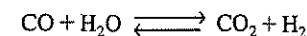
We need $V(X)$ to obtain $C_j = h_j(X)$

We now need only to find volume as a function of conversion to obtain the species concentration as a function of conversion.

3.3.2 Constant-Volume Reaction Systems

Some significant simplifications in the reactor design equations are possible when the reacting system undergoes no change in volume as the reaction progresses. These systems are called constant-volume, or constant-density, because of the invariance of either volume or density during the reaction process. This situation may arise from several causes. In gas-phase batch systems, the reactor is usually a sealed vessel with appropriate instruments to measure pressure and temperature within the reactor. The volume within this vessel is fixed and will not change, and is therefore a constant-volume system. The laboratory bomb reactor is a typical example of this type of reactor.

Another example of a constant-volume gas-phase isothermal reaction occurs when the number of moles of product equals the number of moles of reactant. The water-gas shift reaction, important in coal gasification and many other processes, is one of these:



We want $C_j = h_j(X)$

Batch concentration

In this reaction, 2 mol of reactant forms 2 mol of product. When the number of reactant molecules forms an equal number of product molecules at the *same* temperature and pressure, the volume of the reacting mixture will not change if the conditions are such that the ideal gas law is applicable, or if the compressibility factors of the products and reactants are approximately equal.

For liquid-phase reactions taking place in solution, the solvent usually dominates the situation. As a result, changes in the density of the solute do not affect the overall density of the solution significantly and therefore it is essentially a constant-volume reaction process. Most liquid-phase organic reactions do not change density during the reaction, and represent still another case to which the constant-volume simplifications apply. An important exception to this general rule exists for polymerization processes.

For the constant-volume systems described above, Equation (3-25) can be simplified to give the following expressions relating concentration and conversion:

$$\begin{aligned}
 V &= V_0 \\
 C_A &= \frac{N_{A0}(1-X)}{V_0} = C_{A0}(1-X) \\
 C_B &= \frac{N_{A0}[\Theta_B - (b/a)X]}{V_0} = C_{A0}\left(\Theta_B - \frac{b}{a}X\right) \\
 C_C &= C_{A0}\left(\Theta_C + \frac{c}{a}X\right) \\
 C_D &= C_{A0}\left(\Theta_D + \frac{d}{a}X\right)
 \end{aligned} \quad (3-26)$$

Concentration as a function of conversion when no volume change occurs with reaction

Example 3-4 Expressing $C_j = h_j(X)$ for a Liquid-Phase Reaction

Soap consists of the sodium and potassium salts of various fatty acids such as oleic, stearic, palmitic, lauric, and myristic acids. The saponification for the formation of soap from aqueous caustic soda and glyceryl stearate is

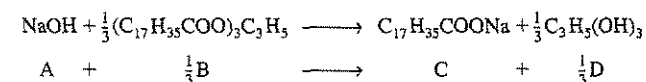


Letting X represent the conversion of sodium hydroxide (the moles of sodium hydroxide reacted per mole of sodium hydroxide initially present), set up a stoichiometric table expressing the concentration of each species in terms of its initial concentration and the conversion X .

Solution

Because we are taking sodium hydroxide as our basis, we divide through by the stoichiometric coefficient of sodium hydroxide to put the reaction expression in the form

Choosing a basis of calculation



We may then perform the calculations shown in Table E3-4.1. Because this is a liquid-phase reaction, the density ρ is considered to be constant; therefore, $V = V_0$.

$$\begin{aligned}
 C_A &= \frac{N_A}{V} = \frac{N_A}{V_0} = \frac{N_{A0}(1-X)}{V_0} = C_{A0}(1-X) \\
 \Theta_B &= \frac{C_{B0}}{C_{A0}} \quad \Theta_C = \frac{C_{C0}}{C_{A0}} \quad \Theta_D = \frac{C_{D0}}{C_{A0}}
 \end{aligned}$$

TABLE E3-4.1. STOICHIOMETRIC TABLE FOR LIQUID-PHASE SOAP REACTION

Species	Symbol	Initially	Change	Remaining	Concentration
NaOH	A	N_{A0}	$-N_{A0}X$	$N_{A0}(1-X)$	$C_{A0}(1-X)$
$(\text{C}_{17}\text{H}_{35}\text{COO})_3\text{C}_3\text{H}_5$	B	N_{B0}	$-\frac{1}{3}N_{A0}X$	$N_{A0}\left(\Theta_B - \frac{X}{3}\right)$	$C_{A0}\left(\Theta_B - \frac{X}{3}\right)$
$\text{C}_{17}\text{H}_{35}\text{COONa}$	C	N_{C0}	$N_{A0}X$	$N_{A0}(\Theta_C + X)$	$C_{A0}(\Theta_C + X)$
$\text{C}_3\text{H}_5(\text{OH})_3$	D	N_{D0}	$\frac{1}{3}N_{A0}X$	$N_{A0}\left(\Theta_D + \frac{X}{3}\right)$	$C_{A0}\left(\Theta_D + \frac{X}{3}\right)$
Water (inert)	I	$\frac{N_{I0}}{N_{T0}}$	$\frac{0}{0}$	$\frac{N_{I0}}{N_T = N_{T0}}$	C_{I0}

Stoichiometric table (batch)

Example 3-5 What Is the Limiting Reactant?

Having set up the stoichiometric table in Example 3-4, one can now readily use it to calculate the concentrations at a given conversion. If the initial mixture consists solely of sodium hydroxide at a concentration of 10 mol/L (i.e., 10 mol/dm³ or 10 kmol/m³) and of glyceryl stearate at a concentration of 2 g mol/L, what is the concentration of glycerine when the conversion of sodium hydroxide is (a) 20% and (b) 90%?

Solution

Only the reactants NaOH and $(\text{C}_{17}\text{H}_{35}\text{COO})_3\text{C}_3\text{H}_5$ are initially present; therefore, $\Theta_C = \Theta_D = 0$.

(a) For 20% conversion:

$$C_D = C_{A0}\left(\frac{X}{3}\right) = (10)\left(\frac{0.2}{3}\right) = 0.67 \text{ g mol/L} = 0.67 \text{ mol/dm}^3$$

$$C_B = C_{A0}\left(\Theta_B - \frac{X}{3}\right) = 10\left(\frac{2}{10} - \frac{0.2}{3}\right) = 10(0.133) = 1.33 \text{ mol/dm}^3$$

(b) For 90% conversion:

$$C_D = C_{A0} \left(\frac{X}{3} \right) = 10 \left(\frac{0.9}{3} \right) = 3 \text{ mol/dm}^3$$

Let us find C_B :

$$C_B = 10 \left(\frac{2}{10} - \frac{0.9}{3} \right) = 10(0.2 - 0.3) = -1 \text{ mol/dm}^3$$

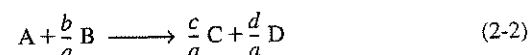
Negative concentration—impossible!

Ninety percent conversion of NaOH is not possible, because glyceryl stearate is the limiting reactant. Consequently, all the glyceryl stearate is used up before 90% of the NaOH could be reacted. It is important to choose the limiting reactant as the basis of calculation.

The basis of calculation should be the limiting reactant

3.3.3 Flow Systems

The form of the stoichiometric table for a continuous-flow system (see Figure 3-2) is virtually identical to that for a batch system (Table 3-2) except that we replace N_{j0} by F_{j0} and N_j by F_j (Table 3-3). Taking A as the basis, divide Equation (2-1) through by the stoichiometric coefficient of A to obtain



For a flow system, the concentration C_A at a given point can be determined from F_A and the volumetric flow rate v at that point:

$$C_A = \frac{F_A}{v} = \frac{\text{moles/time}}{\text{liters/time}} = \frac{\text{moles}}{\text{liter}} \quad (3-27)$$

Definition of concentration for flow system

Units of v are typically given in terms of liters per second, cubic decimeters per second, or cubic feet per minute. We now can write the concentrations of A, B, C, and D for the general reaction given by Equation (2-2) in terms of the entering molar flow rate (F_{A0} , F_{B0} , F_{C0} , F_{D0}), the conversion X , and the volumetric flow rate, v .

$$\begin{aligned} C_A &= \frac{F_A}{v} = \frac{F_{A0}}{v} (1 - X) & C_B &= \frac{F_B}{v} = \frac{F_{B0} - (b/a) F_{A0} X}{v} \\ C_C &= \frac{F_C}{v} = \frac{F_{C0} + (c/a) F_{A0} X}{v} & C_D &= \frac{F_D}{v} = \frac{F_{D0} + (d/a) F_{A0} X}{v} \end{aligned} \quad (3-28)$$

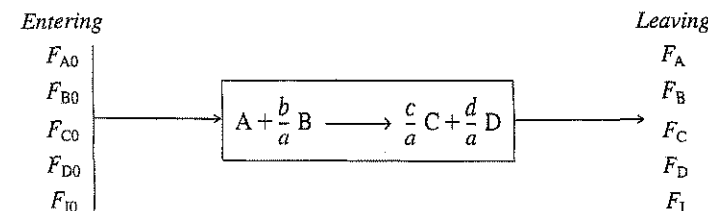


Figure 3-2 Flow reactor.

where

$$\Theta_B = \frac{F_{B0}}{F_{A0}} = \frac{C_{B0} v_0}{C_{A0} v_0} = \frac{C_{B0}}{C_{A0}} = \frac{y_{B0}}{y_{A0}}$$

and Θ_C , Θ_D , and Θ_I are defined similarly.

TABLE 3-3. STOICHIOMETRIC TABLE FOR A FLOW SYSTEM

Species	Feed Rate to Reactor (mol/time)	Change within Reactor (mol/time)	Effluent Rate from Reactor (mol/time)
A	F_{A0}	$-F_{A0}X$	$F_A = F_{A0}(1 - X)$
B	$F_{B0} = \Theta_B F_{A0}$	$-\frac{b}{a} F_{A0} X$	$F_B = F_{A0} \left(\Theta_B - \frac{b}{a} X \right)$
C	$F_{C0} = \Theta_C F_{A0}$	$\frac{c}{a} F_{A0} X$	$F_C = F_{A0} \left(\Theta_C + \frac{c}{a} X \right)$
D	$F_{D0} = \Theta_D F_{A0}$	$\frac{d}{a} F_{A0} X$	$F_D = F_{A0} \left(\Theta_D + \frac{d}{a} X \right)$
I	$F_{I0} = \Theta_I F_{A0}$	—	$F_I = F_{A0} \Theta_I$
	F_{T0}		$F_T = F_{T0} + \left(\frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1 \right) F_{A0} X$ $F_T = F_{T0} + \delta F_{A0} X$

Stoichiometric table (flow)

For liquids, volume change with reaction is negligible when no phase changes are taking place. Consequently, we can take

$$v = v_0$$

For liquids Then

$$C_A = C_{A0}(1 - X)$$

$$C_B = C_{A0} \left(\Theta_B - \frac{b}{a} X \right)$$

Therefore, for a given rate law we have $-r_A = g(X)$

$$C_A = \frac{F_{A0}}{v_0} (1 - X) = C_{A0}(1 - X) \quad (3-29)$$

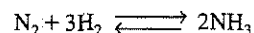
$$C_B = C_{A0} \left(\Theta_B - \frac{b}{a} X \right) \text{ etc.}$$

However, for gas-phase reactions the volumetric flow rate most often changes during the course of the reaction due to a change in the total number of moles or in temperature or pressure. One cannot always use Equation (3-29) to express concentration as a function of conversion for gas-phase reactions.

3.3.4 Volume Change with Reaction

In our previous discussions, we considered primarily systems in which the reaction volume or volumetric flow rate did not vary as the reaction progressed. Most batch and liquid-phase and some gas-phase systems fall into this category. There are other systems, though, in which either V or v do vary, and these will now be considered.

A situation in which a varying flow rate occurs quite frequently is in gas-phase reactions that do not have an equal number of product and reactant moles. For example, in the synthesis of ammonia,



4 mol of reactants gives 2 mol of product. In flow systems where this type of reaction occurs, the molar flow rate will be changing as the reaction progresses. Because only equal numbers of moles occupy equal volumes in the gas phase at the same temperature and pressure, the volumetric flow rate will also change.

Another variable-volume situation, which occurs much less frequently, is in batch reactors where volume changes with time. Examples of this situation are the combustion chamber of the internal-combustion engine and the expanding gases within the breech and barrel of a firearm as it is fired.

In the stoichiometric tables presented on the preceding pages, it was not necessary to make assumptions concerning a volume change in the first four columns of the table (i.e., the species, initial number of moles or molar feed rate, change within the reactor, and the remaining number of moles or the molar effluent rate). All of these columns of the stoichiometric table are independent of the volume or density and they are *identical* for constant-volume (constant-density) and varying-volume (varying-density) situations. Only when concentration is expressed as a function of conversion does variable density enter the picture.

Individual concentrations can be determined by expressing the volume V for a batch system (or volumetric flow rate v for a flow system) as a function of conversion using the following equation of state:

Equation of state

$$PV = ZN_T RT \quad (3-30)$$

in which V and N_T are defined as before and

T = temperature, K

P = total pressure, atm (kPa; 1 atm = 101.3 kPa)

Z = compressibility factor

R = gas constant = $0.08206 \text{ dm}^3 \cdot \text{atm/g mol} \cdot \text{K}$

This equation is valid at any point in the system at any time t . At time $t = 0$ (i.e., when the reaction is initiated), Equation (3-30) becomes

$$P_0 V_0 = Z_0 N_{T0} R T_0 \quad (3-31)$$

Dividing Equation (3-30) by Equation (3-31) and rearranging yields

$$V = V_0 \left(\frac{P_0}{P} \right) \frac{T}{T_0} \left(\frac{Z}{Z_0} \right) \frac{N_T}{N_{T0}} \quad (3-32)$$

We now want to express the volume V as a function of the conversion X . Recalling the equation for the total number of moles in Table 3-2,

$$N_T = N_{T0} + \delta N_{A0} X \quad (3-33)$$

we divide through by N_{T0} :

$$\frac{N_T}{N_{T0}} = 1 + \frac{N_{A0}}{N_{T0}} \delta X = 1 + \delta y_{A0} X \quad (3-34)$$

where y_{A0} is the mole fraction of A initially present. If all the species in the generalized reaction are in the gas phase, then

$$\delta = \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1 \quad (3-23)$$

Equation (3-34) is further simplified by letting

$$\varepsilon = \frac{\text{change in total number of moles for complete conversion}}{\text{total number of moles fed to the reactor}}$$

Definitions of δ and ε In symbols,

$$\varepsilon = \left(\frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1 \right) \frac{N_{A0}}{N_{T0}} = y_{A0} \delta \quad (3-35)$$

$$\varepsilon = y_{A0} \delta \quad (3-36)$$

Equation (3-32) now becomes

$$V = V_0 \left(\frac{P_0}{P} \right) \frac{T}{T_0} \left(\frac{Z}{Z_0} \right) (1 + \varepsilon X) \quad (3-37)$$

In gas-phase systems that we shall be studying, the temperatures and pressures are such that the compressibility factor will not change significantly during the course of the reaction; hence $Z_0 \cong Z$. For a batch system the volume of gas at any time t is

Volume of gas for
a variable volume
batch reaction

$$V = V_0 \left(\frac{P_0}{P} \right) (1 + \varepsilon X) \frac{T}{T_0} \quad (3-38)$$

Equation (3-38) applies only to a *variable-volume* batch reactor. If the reactor is a rigid steel container of constant volume, then of course $V = V_0$. For a constant-volume container, $V = V_0$, and Equation (3-38) can be used to calculate the pressure inside the reactor as a function of temperature and conversion.

An expression similar to Equation (3-38) for a variable-volume batch reactor exists for a variable-volume flow system. To derive the concentrations of the species in terms of conversion for a variable-volume flow system, we shall use the relationships for the total concentration. The total concentration at any point in the reactor is

$$C_T = \frac{F_T}{v} = \frac{P}{ZRT} \quad (3-39)$$

At the entrance to the reactor,

$$C_{T0} = \frac{F_{T0}}{v_0} = \frac{P_0}{Z_0 R T_0} \quad (3-40)$$

Taking the ratio of Equation (3-40) to Equation (3-39) and assuming negligible changes in the compressibility factor, we have upon rearrangement

$$v = v_0 \left(\frac{F_T}{F_{T0}} \right) \frac{P_0}{P} \left(\frac{T}{T_0} \right) \quad (3-41)$$

From Table 3-3, the total molar flow rate is

$$F_T = F_{T0} + F_{A0} \delta X \quad (3-42)$$

Substituting for F_T in Equation (3-41) gives

$$\begin{aligned} v &= v_0 \frac{F_{T0} + F_{A0} \delta X}{F_{T0}} \left(\frac{P_0}{P} \right) \frac{T}{T_0} \\ &= v_0 \left(1 + \frac{F_{A0}}{F_{T0}} \delta X \right) \frac{P_0}{P} \left(\frac{T}{T_0} \right) = v_0 (1 + y_{A0} \delta X) \frac{P_0}{P} \left(\frac{T}{T_0} \right) \end{aligned} \quad (3-43)$$

Gas-phase
volumetric flow
rate

$$v = v_0 (1 + \varepsilon X) \frac{P_0}{P} \left(\frac{T}{T_0} \right) \quad (3-44)$$

We can now express the concentration of species j for a flow system in terms of conversion:

$$C_j = \frac{F_j}{v} = \frac{F_j}{v_0 \left(\frac{F_T}{F_{T0}} \right) \frac{P_0}{P} \frac{T}{T_0}} = \left(\frac{F_{T0}}{v_0} \right) \left(\frac{F_j}{F_T} \right) \left(\frac{P}{P_0} \right) \left(\frac{T_0}{T} \right)$$

For multiple
reactions
(Chapter 6)

$$C_j = C_{T0} \left(\frac{F_j}{F_T} \right) \left(\frac{P}{P_0} \right) \left(\frac{T_0}{T} \right) \quad (3-45)$$

We will use this form of the concentration equation for multiple gas-phase reactions and for membrane reactors. Substituting for F_j and F_T in terms of conversion in Equation (3-45) yields

$$C_j = C_{T0} \frac{F_{A0} (\Theta_j + \nu_j X)}{F_{T0} + F_{A0} \delta X} \left(\frac{P}{P_0} \right) \left(\frac{T_0}{T} \right)$$

Dividing numerator and denominator by F_{T0} , we have

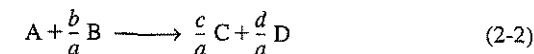
$$C_j = C_{T0} \left(\frac{F_{A0}}{F_{T0}} \right) \frac{\Theta_j + \nu_j X}{1 + (F_{A0}/F_{T0}) \delta X} \left(\frac{P}{P_0} \right) \left(\frac{T_0}{T} \right)$$

Recalling $y_{A0} = F_{A0}/F_{T0}$ and $C_{A0} = y_{A0} C_{T0}$, then

Gas-phase
concentration as a
function of
conversion

$$C_j = \frac{C_{A0} (\Theta_j + \nu_j X)}{1 + \varepsilon X} \left(\frac{P}{P_0} \right) \frac{T_0}{T} \quad (3-46)$$

where ν_j is the stoichiometric coefficient, which is negative for reactants and positive for products. For example, for the reaction



$\nu_A = -1$, $\nu_B = -b/a$, $\nu_C = c/a$, and $\nu_D = d/a$.

The stoichiometry table for the gas-phase reaction (2-2) is given in Table 3-4.

TABLE 3-4. CONCENTRATIONS IN A VARIABLE-VOLUME GAS FLOW SYSTEM

$$\begin{aligned}
 C_A &= \frac{F_A}{v} = \frac{F_{A0}(1-X)}{v} = \frac{F_{A0}(1-X)}{v_0(1+\varepsilon X)} \left(\frac{T_0}{T} \right) \frac{P}{P_0} = C_{A0} \left(\frac{1-X}{1+\varepsilon X} \right) \frac{T_0}{T} \left(\frac{P}{P_0} \right) \\
 C_B &= \frac{F_B}{v} = \frac{F_{A0}[\Theta_B - (b/a)X]}{v} = \frac{F_{A0}[\Theta_B - (b/a)X]}{v_0(1+\varepsilon X)} \left(\frac{T_0}{T} \right) \frac{P}{P_0} = C_{A0} \left(\frac{\Theta_B - (b/a)X}{1+\varepsilon X} \right) \frac{T_0}{T} \left(\frac{P}{P_0} \right) \\
 C_C &= \frac{F_C}{v} = \frac{F_{A0}[\Theta_C + (c/a)X]}{v} = \frac{F_{A0}[\Theta_C + (c/a)X]}{v_0(1+\varepsilon X)} \left(\frac{T_0}{T} \right) \frac{P}{P_0} = C_{A0} \left(\frac{\Theta_C + (c/a)X}{1+\varepsilon X} \right) \frac{T_0}{T} \left(\frac{P}{P_0} \right) \\
 C_D &= \frac{F_D}{v} = \frac{F_{A0}[\Theta_D + (d/a)X]}{v} = \frac{F_{A0}[\Theta_D + (d/a)X]}{v_0(1+\varepsilon X)} \left(\frac{T_0}{T} \right) \frac{P}{P_0} = C_{A0} \left(\frac{\Theta_D + (d/a)X}{1+\varepsilon X} \right) \frac{T_0}{T} \left(\frac{P}{P_0} \right) \\
 C_I &= \frac{F_I}{v} = \frac{F_{A0}\Theta_I}{v} = \frac{F_{A0}\Theta_I}{v_0(1+\varepsilon X)} \left(\frac{T_0}{T} \right) \frac{P}{P_0} = \frac{C_{A0}\Theta_I}{1+\varepsilon X} \left(\frac{T_0}{T} \right) \frac{P}{P_0}
 \end{aligned}$$

At last!
We now have
 $C_i = h_i(X)$
and
 $-r_A = g(X)$
for variable-volume
gas-phase reactions

Example 3-6 Manipulation of the Equation for $C_i = h_i(X)$

Show under what conditions and manipulation the expression for C_B for a gas flow system reduces to that given in Table 3-4.

Solution

For a flow system the concentration is defined as

$$C_B = \frac{F_B}{v} \quad (\text{E3-6.1})$$

From Table 3-3, the molar flow rate and conversion are related by

$$F_B = F_{A0} \left(\Theta_B - \frac{b}{a} X \right) \quad (\text{E3-6.2})$$

Combining Equations (E3-6.1) and (E3-6.2) yields

$$C_B = \frac{F_{A0}[\Theta_B - (b/a)X]}{v} \quad (\text{E3-6.3})$$

Using Equation (3-44) gives us

$$v = v_0(1 + \varepsilon X) \frac{P_0}{P} \left(\frac{T}{T_0} \right) \quad (3-44)$$

to substitute for the volumetric flow rate gives

$$C_B = \frac{F_B}{v} = \frac{F_{A0}[\Theta_B - (b/a)X]}{v_0(1 + \varepsilon X)} \left(\frac{P}{P_0} \right) \frac{T_0}{T} \quad (\text{E3-6.4})$$

Recalling $\frac{F_{A0}}{v_0} = C_{A0}$, we obtain

This equation for v
is only for a gas-
phase reaction

$$C_B = C_{A0} \left[\frac{\Theta_B - (b/a)X}{1 + \varepsilon X} \right] \frac{P}{P_0} \left(\frac{T_0}{T} \right)$$

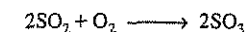
which is identical to the concentration expression for a variable-volume batch reactor.

Similarly, substituting ε and the appropriate Θ 's into different concentration expressions for a flow system gives the same concentration expressions as those in Table 3-4 for a variable-volume batch reaction in the gas phase.

One of the major objectives of this chapter is to learn how to express any given rate law $-r_A$ as a function of conversion. The schematic diagram in Figure 3-3 helps to summarize our discussion on this point. The concentration of the key reactant, A (the basis of our calculations), is expressed as a function of conversion in both flow and batch systems, for various conditions of temperature, pressure, and volume.

Example 3-7 Determining $C_i = h_i(X)$ for a Gas-Phase Reaction

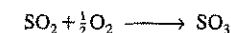
A mixture of 28% SO_2 and 72% air is charged to a flow reactor in which SO_2 is oxidized.



First, set up a stoichiometric table using only the symbols (i.e., Θ_i , F_i) and then prepare a second stoichiometric table evaluating numerically as many symbols as possible for the case when the total pressure is 1485 kPa and the temperature is constant at 227°C.

Solution

Taking SO_2 as the basis of calculation, we divide the reaction through by the stoichiometric coefficient of our chosen basis of calculation:



The initial stoichiometric table is given as Table E3-7.1. Initially, 72% of the total number of moles is air containing 21% O_2 and 79% N_2 .

$$F_{A0} = (0.28)(F_{T0})$$

$$F_{B0} = (0.72)(0.21)(F_{T0})$$

$$\Theta_B = \frac{F_{B0}}{F_{A0}} = \frac{(0.72)(0.21)}{0.28} = 0.54$$

$$\Theta_1 = \frac{F_{I0}}{F_{A0}} = \frac{(0.72)(0.79)}{0.28} = 2.03$$

To write concentration in terms of conversion, we must express the volumetric flow rate as a function of conversion.

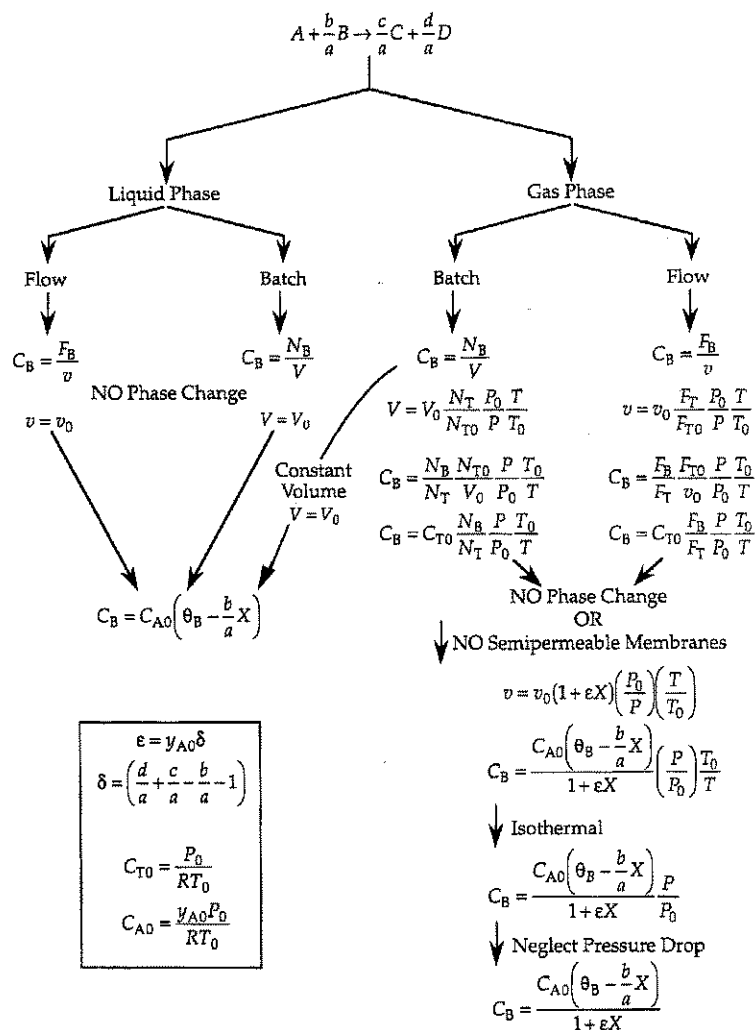


Figure 3-3 Expressing concentration as a function of conversion.

TABLE E3-7.1. STOICHIOMETRIC TABLE FOR $\text{SO}_2 + \frac{1}{2}\text{O}_2 \longrightarrow \text{SO}_3$

Species	Symbol	Initially	Change	Remaining
SO_2	A	F_{A0}	$-F_{A0}X$	$F_A = F_{A0}(1 - X)$
O_2	B	$F_{B0} = \Theta_B F_{A0}$	$-\frac{F_{A0}X}{2}$	$F_B = F_{A0} \left(\Theta_B - \frac{1}{2}X \right)$
SO_3	C	0	$+F_{A0}X$	$F_C = F_{A0}X$
N_2	I	$\frac{F_{I0} = \Theta_I F_{A0}}{F_{T0}}$	—	$F_I = F_{I0} = \Theta_I F_{A0}$ $F_T = F_{T0} - \frac{F_{A0}X}{2}$

$$C_A = \frac{F_A}{v} = \frac{F_{A0}(1 - X)}{v}$$

Recalling Equation (3-44), we have

$$v = v_0(1 + \epsilon X) \frac{P_0}{P} \left(\frac{T}{T_0} \right)$$

Neglecting pressure drop in the reaction, $P = P_0$, yields

$$v = v_0(1 + \epsilon X) \frac{T}{T_0}$$

If the reaction is also carried out isothermally, $T = T_0$, we obtain

$$v = v_0(1 + \epsilon X)$$

$$C_A = \frac{F_{A0}(1 - X)}{v_0(1 + \epsilon X)} = C_{A0} \left(\frac{1 - X}{1 + \epsilon X} \right)$$

The concentration of A initially is equal to the mole fraction of A initially multiplied by the total concentration. The total concentration can be calculated from an equation of state such as the ideal gas law:

$$\begin{aligned}
 C_{A0} &= y_{A0} C_{T0} = y_{A0} \left(\frac{P_0}{RT_0} \right) \\
 &= 0.28 \left(\frac{1485 \text{ kPa}}{8.314 \text{ kPa} \cdot \text{dm}^3/\text{mol} \cdot \text{K} \times 500 \text{ K}} \right) \\
 &= 0.1 \text{ mol/dm}^3
 \end{aligned}$$

The total concentration is

$$C_T = \frac{F_T}{v} = \frac{F_{T0} + y_{A0} \delta X F_{T0}}{v_0(1 + \varepsilon X)} = \frac{F_{T0}(1 + \varepsilon X)}{v_0(1 + \varepsilon X)} = \frac{F_{T0}}{v_0} = C_{T0} = \frac{P_0}{RT_0}$$

$$= \frac{1485 \text{ kPa}}{(8.314 \text{ kPa} \cdot \text{dm}^3/\text{mol} \cdot \text{K})(500 \text{ K})} = 0.357 \frac{\text{mol}}{\text{dm}^3}$$

We now evaluate ε .

$$\varepsilon = y_{A0} \delta = (0.28)(1 - 1 - \frac{1}{2}) = -0.14$$

$$C_A = C_{A0} \left(\frac{1-X}{1+\varepsilon X} \right) = 0.1 \left(\frac{1-X}{1-0.14X} \right) \text{ mol/dm}^3$$

$$C_B = C_{A0} \left(\frac{\Theta_B - \frac{1}{2}X}{1+\varepsilon X} \right) = \frac{0.1(0.54 - 0.5X)}{1-0.14X} \text{ mol/dm}^3$$

$$C_C = \frac{C_{A0}X}{1+\varepsilon X} = \frac{0.1X}{1-0.14X} \text{ mol/dm}^3$$

$$C_I = \frac{C_{A0}\Theta_I}{1+\varepsilon X} = \frac{(0.1)(2.03)}{1-0.14X} \text{ mol/dm}^3$$

The concentrations of different species at various conversions are calculated in Table E3-7.2 and plotted in Figure E3-7.1. Note that the concentration of N_2 is changing even though it is an inert species in this reaction.

TABLE E3-7.2. CONCENTRATION AS A FUNCTION OF CONVERSION

Species		$C_i \text{ (g mol/dm}^3\text{)}$				
		$X = 0.0$	$X = 0.25$	$X = 0.5$	$X = 0.75$	$X = 1.0$
SO_2	$C_A =$	0.100	0.078	0.054	0.028	0.000
O_2	$C_B =$	0.054	0.043	0.031	0.018	0.005
SO_3	$C_C =$	0.000	0.026	0.054	0.084	0.116
N_2	$C_I =$	0.203	0.210	0.218	0.227	0.236
	$C_T =$	0.357	0.357	0.357	0.357	0.357

We are now in a position to express $-r_A$ as a function of X . For example, if the rate law for this reaction were first order in SO_2 (i.e., A) and in O_2 (i.e., B), with $k = 200 \text{ dm}^3/\text{mol} \cdot \text{s}$, then the rate law becomes

$$-r_A = kC_A C_B = kC_{A0}^2 \frac{(1-X)(\Theta_B - 0.5X)}{(1+\varepsilon X)^2} = \frac{2(1-X)(0.54 - 0.5X)}{(1-0.14X)^2} \quad (\text{E3-7.1})$$

Taking the reciprocal of $-r_A$ yields

$$\frac{1}{-r_A} = \frac{0.5(1-0.14X)^2}{(1-X)(0.54-0.5X)} \quad (\text{E3-7.2})$$

Use Eq. (E3-7.2) to obtain

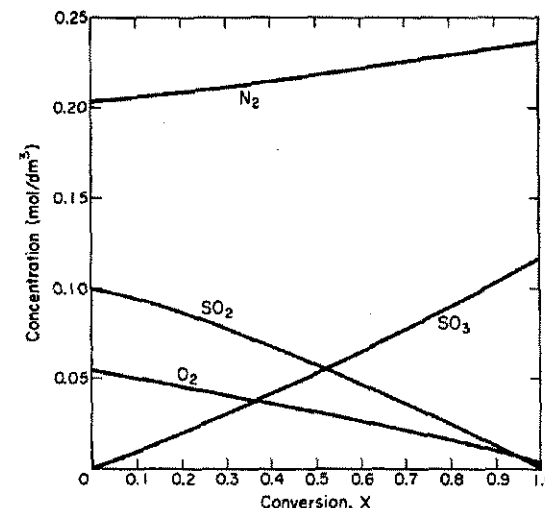
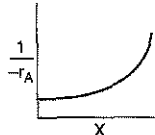


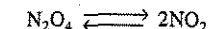
Figure E3-7.1 Concentration as a function of conversion.

We see that we could size a variety of combinations of *isothermal reactors* using the techniques discussed in Chapter 2.

All the reactions used thus far in this chapter have been irreversible reactions. The procedure one uses for the isothermal reactor design of reversible reactions is virtually the same as that for irreversible reactions, with one notable exception. First calculate the maximum conversion that can be achieved at the isothermal reaction temperature. This value is the equilibrium conversion. In the following example it will be shown how our algorithm for reactor design is easily extended to reversible reactions.

Example 3-8 Calculating the Equilibrium Conversion

The reversible gas-phase decomposition of nitrogen tetroxide, N_2O_4 , to nitrogen dioxide, NO_2 ,

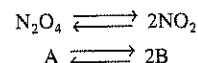


is to be carried out at constant temperature and pressure. The feed consists of pure N_2O_4 at 340 K and 2 atm. The concentration equilibrium constant at 340 K is 0.1 mol/dm^3 .

- Calculate the equilibrium conversion of N_2O_4 in a constant-volume batch reactor.
- Calculate the equilibrium conversion of N_2O_4 in a flow reactor.

- (c) Assuming the reaction is elementary, express the rate of reaction solely as a function of conversion for a flow system and for a batch system.

Solution



At equilibrium the concentrations of the reacting species are related by the relationship dictated by thermodynamics [see Equation (3-10) and Appendix C]

$$K_C = \frac{C_{\text{Be}}^2}{C_{\text{Ac}}} \quad (\text{E3-8.1})$$

- (a) Batch system—constant volume, $V = V_0$. See Table E3-8.1.

TABLE E3-8.1. STOICHIOMETRIC TABLE

Species	Symbol	Initial	Change	Remaining
N ₂ O ₄	A	N _{A0}	-N _{A0} X	N _A = N _{A0} (1 - X)
NO ₂	B	0	+2N _{A0} X	N _B = 2N _{A0} X
		N _{T0} = N _{A0}		N _T = N _{T0} + N _{A0} X

For batch systems $C_i = N_i/V$,

$$C_A = \frac{N_A}{V} = \frac{N_A}{V_0} = \frac{N_{A0}(1-X)}{V_0} = C_{A0}(1-X) \quad (\text{E3-8.2})$$

$$C_B = \frac{N_B}{V} = \frac{N_B}{V_0} = \frac{2N_{A0}X}{V_0} = 2C_{A0}X \quad (\text{E3-8.3})$$

$$\begin{aligned} C_{A0} &= \frac{y_{A0}P_0}{RT_0} = \frac{(1)(2 \text{ atm})}{(0.082 \text{ atm} \cdot \text{dm}^3/\text{gmol} \cdot \text{K})(340 \text{ K})} \\ &= 0.07174 \text{ mol/dm}^3 \end{aligned}$$

At equilibrium $X = X_e$ and we substitute Equations (E3-8.2) and (E3-8.3) into Equation (E3-8.1),

$$\begin{aligned} K_C &= \frac{C_{\text{Be}}^2}{C_{\text{Ac}}} = \frac{4C_{A0}^2X_e^2}{C_{A0}(1-X_e)} = \frac{4C_{A0}X_e^2}{1-X_e} \\ X_e &= \sqrt{\frac{K_C(1-X_e)}{4C_{A0}}} \quad (\text{E3-8.4}) \end{aligned}$$

We will use POLYMATH to solve for the equilibrium conversion and let xeb represent the equilibrium conversion in a constant-volume batch reactor. Equation (E3-8.4) written in POLYMATH format becomes

$$f(\text{xeb}) = \text{xeb} - [\text{kc} \cdot (1 - \text{xeb}) / (4 \cdot \text{cao})] ** 0.5$$

The POLYMATH program and solution are given in Tables E3-8.2 and E3-8.3. The equilibrium conversion in a constant-volume batch reactor is

$$X_{\text{eb}} = 0.44$$

TABLE E3-8.2. POLYMATH PROGRAM

Equations:	Initial Values:
f(Xeb)=Xeb-(Kc*(1-Xeb)/(4*Xcao))**0.5	0.5
f(Xef)=Xef-(Kc*(1-Xef)/(1+eps*Xef)/(4*Xcao))**0.5	0.5
Kc=0.1	
Cao=0.07174	
eps=1	

TABLE E3-8.3. POLYMATH SOLUTION

N2O4 EQUILIBRIUM CONVERSION FOR BATCH AND FLOW SYSTEMS

Variable	Solution Value	f()
Xeb	0.44126	3.661e-16
Xef	0.508355	-3.274e-17
Kc	0.1	
Cao	0.07174	
eps	1	

(b) Flow system. The stoichiometric table is the same as that for a batch system except that the number of moles of each species, N_i , is replaced by the molar flow rate of that species, F_i . For constant temperature and pressure the volumetric flow rate is $v = v_0(1 + \epsilon X)$ and the resulting concentrations of species A and B are

$$C_A = \frac{F_A}{v} = \frac{F_{A0}(1-X)}{v} = \frac{F_{A0}(1-X)}{v_0(1+\epsilon X)} = \frac{C_{A0}(1-X)}{1+\epsilon X} \quad (\text{E3-8.5})$$

$$C_B = \frac{F_B}{v} = \frac{2F_{A0}X}{v_0(1+\epsilon X)} = \frac{2C_{A0}X}{1+\epsilon X} \quad (\text{E3-8.6})$$

At equilibrium $X = X_e$ and we can substitute Equations (E3-8.5) and (E3-8.6) into Equation (E3-8.1) to obtain the expression

$$K_C = \frac{C_{\text{Be}}^2}{C_{\text{Ac}}} = \frac{[2C_{A0}X_e/(1+\epsilon X_e)]^2}{C_{A0}(1-X_e)/(1+\epsilon X_e)}$$

Simplifying gives

$$K_C = \frac{4C_{A0}X_e^2}{(1-X_e)(1+\epsilon X_e)} \quad (\text{E3-8.7})$$

Rearranging to use POLYMATH yields

$$X_e = \sqrt{\frac{K_C(1-X_e)(1+\varepsilon X_e)}{4C_{A0}}} \quad (\text{E3-8.8})$$

For a pure N_2O_4 feed, $\varepsilon = y_{A0} \delta = 1(2-1) = 1$.

We shall let x_{ef} represent the equilibrium conversion in a flow system. Equation (E3-8.8) written in the POLYMATH format becomes

$$f(x_{ef}) = x_{ef} - [k_c(1-x_{ef})(1+\varepsilon x_{ef})/4C_{A0}]^{0.5}$$

This solution is also shown in Tables E3-8.2 and E3-8.3.

Note that the equilibrium conversion in a flow reactor (i.e., $X_{ef} = 0.51$), with negligible pressure drop, is greater than the equilibrium conversion in a constant-volume batch reactor ($X_{eb} = 0.44$). Recalling Le Châtelier's principle, can you suggest an explanation for this difference in X_e ?

(c) **Rate laws.** Assuming that the reaction follows an elementary rate law, then

$$-r_A = k_A \left[C_A - \frac{C_B}{K_C} \right] \quad (\text{E3-8.9})$$

1. For a flow system, $C_A = F_A/v$ and $C_B = F_B/v$ with $v = v_0(1+\varepsilon X)$. Consequently, we can substitute Equations (E3-8.5) and (E3-8.6) into Equation (E3-8.9) to obtain

$$-r_A = k_A \left[\frac{C_{A0}(1-X)}{1+\varepsilon X} - \frac{4C_{A0}^2 X^2}{K_C(1+\varepsilon X)^2} \right] \quad (\text{E3-8.10})$$

Let's check to see if at equilibrium this equation reduces to the same equation as that obtained from thermodynamics. At equilibrium $-r_A = 0$:

$$0 = \frac{k_A C_{A0}}{1+\varepsilon X_e} \left[1 - X_e - \frac{4C_{A0} X_e^2}{K_C(1+\varepsilon X_e)} \right]$$

Rearranging gives us

$$X_e = \sqrt{\frac{K_C(1-X_e)(1+\varepsilon X_e)}{4C_{A0}}} \quad (\text{E3-8.8})$$

It **must** agree with the value calculated from thermodynamic value and it does!

2. For a constant volume ($V = V_0$) batch system, $C_A = N_A/V_0$ and $C_B = N_B/V_0$. Substituting Equations (E3-8.2) and (E3-8.3) into the rate law, we obtain the rate of disappearance of A as a function of conversion:

$$-r_A = k_A \left[C_A - \frac{C_B}{K_C} \right] = k_A \left[C_{A0}(1-X) - \frac{4C_{A0}^2 X^2}{K_C} \right] \quad (\text{E3-8.11})$$

$-r_A = f(X)$
for a batch reactor
with $V = V_0$

$-r_A = f(X)$ for a
flow reactor

As expected, the dependence of reaction rate on conversion for a constant-volume batch system [i.e., Equation (E3-8.11)] is different than that for a flow system [Equation (E3-8.10)] for gas-phase reactions.

3.4 Expressing Concentrations in Terms Other Than Conversion

As we shall see later in the book, there are some instances in which it is much more convenient to work in terms of the number of moles (N_A, N_B) or molar flow rates (F_A, F_B , etc.) rather than conversion. Membrane reactors and gas-phase multiple reactions are two such cases where molar flow rates rather than conversion are preferred. Consequently, the concentrations in the rate laws need to be expressed in terms of the molar flow rates. We start by recalling and combining Equations (3-40) and (3-41):

$$C_{T0} = \frac{F_{T0}}{v_0} = \frac{P_0}{Z_0 R T_0}$$

$$v = \left(\frac{v_0}{F_{T0}} \right) F_T \frac{P_0}{P} \frac{T}{T_0}$$

Used for:
• Multiple rxns
• Membranes
• Unsteady state

to give

$$v = \frac{F_T}{C_{T0}} \frac{P_0}{P} \frac{T}{T_0} \quad (\text{3-47})$$

For the case of an ideal gas ($Z = 1$), the concentration is

$$C_A = \frac{F_A}{v}$$

Substituting for v gives

$$C_A = C_{T0} \frac{F_A}{F_T} \frac{P}{P_0} \frac{T_0}{T} \quad (\text{3-48})$$

In general ($j = A, B, C, D, I$)

$$C_j = C_{T0} \frac{F_j}{F_T} \frac{P}{P_0} \frac{T_0}{T} \quad (\text{3-49})$$

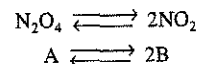
with the total molar flow rate given as the sum of the flow rates of the individual species:

$$F_T = F_A + F_B + F_C + F_D + F_I \quad (\text{3-49})$$

The molar flow rate of each species F_j is obtained from a mole balance on each species.

Example 3-9 PFR Mole Balances in Terms of Molar Flow Rates

Reconsider the elementary gas reaction discussed in Example 3-8.



The reaction is to be carried out isothermally ($T = T_0$) and isobarically ($P = P_0$) in a PFR. Express the rate law and mole balances in terms of the molar flow rates.

Solution

Mole balance: $\frac{dF_A}{dV} = r_A$ (E3-9.1)

$\frac{dF_B}{dV} = r_B$ (E3-9.2)

Rate law: $-r_A = k_A \left[C_A - \frac{C_B^2}{K_C} \right]$ (E3-9.3)

Stoichiometry: $\frac{r_A}{-1} = \frac{r_B}{2}$

Then

$r_B = -2r_A$ (E3-9.4)

Combine:

Using Equation (3-45) to substitute for the concentrations of A and B when $T = T_0$ and $P = P_0$, Equation (E3-9.3) becomes

$-r_A = k_A \left[C_{T0} \left(\frac{F_A}{F_T} \right) - \frac{C_{T0}^2}{K_C} \left(\frac{F_B}{F_T} \right)^2 \right]$ (E3-9.5)

where the total molar flow rate is just the sum of the flow rates of A and B:

$F_T = F_A + F_B$ (E3-9.6)

and the total concentration of the entrance to the reactor (P_0, T_0) is calculated from the equation

$C_{T0} = \frac{P_0}{RT_0}$ (E3-9.7)

Combining Equations (E3-9.5) and (E3-9.6), we obtain

$\frac{dF_A}{dV} = r_A = -k_A C_{T0} \left[\frac{F_A}{F_A + F_B} - \frac{C_{T0}}{K_C} \left(\frac{F_B}{F_A + F_B} \right)^2 \right]$ (E3-9.8)

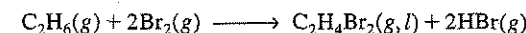
and combining Equations (E3-9.2), (E3-9.4), and (E3-9.8) gives

$\frac{dF_B}{dV} = r_B = -2r_A = 2k_A C_{T0} \left[\frac{F_A}{F_A + F_B} - \frac{C_{T0}}{K_C} \left(\frac{F_B}{F_A + F_B} \right)^2 \right]$ (E3-9.9)

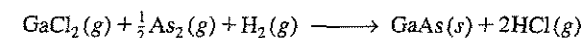
Equations (E3-9.8) and (E3-9.9) can now be solved numerically, preferably by a software package such as POLYMATH or MATLAB. (See Chapter 4)

3.5 Reactions with Phase Change

When Equation (3-36) is used to evaluate ε , it should be remembered from the derivation of this equation that δ represents the change in the number of moles in the gas phase per mole of A reacted. As the last example in this chapter, we consider a gas-phase reaction in which condensation occurs. An example of this class of reactions is

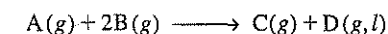


Another example of phase change during reaction is chemical vapor deposition (CVD), a process used to manufacture microelectronic materials. Here, gas-phase reactants are deposited (analogous to condensation) as thin films on solid surfaces (see Problem P3-25). One such reaction is the production of gallium arsenide, which is used in computer chips.



The development of continuous-flow CVD reactors where solid wafers and gases continuously pass through the reactor is currently under way (see Sections 10.8 and 12.10).

We now will develop our stoichiometric table for reactions with phase change. When one of the products condenses during the course of a reaction, calculation of the change in volume or volumetric flow rate must be undertaken in a slightly different manner. Consider another isothermal reaction:



The vapor pressure of species D at temperature T is P_v .

The gas-phase concentration of the product D will increase until the corresponding mole fraction at which condensation begins is reached:

$y_{D,e} = \frac{P_v}{P_T}$ (3-50)

At $P_D = P_v$,
 $y_D = y_{D,e}$ and
condensation starts

Once saturation is reached in the gas phase, every mole of D produced condenses. To account for the effects of condensation on the concentrations of the reacting species, we now write two columns for the number of moles (or molar

flow rates) in our stoichiometric table (Table 3-5). One column gives the molar flow rates of each species before condensation has begun and the other column gives these quantities after condensation has begun. We use X_c to refer to the conversion of A at which the condensation of D begins. Note that we must rearrange the equation for the total molar flow rate to write it explicitly in terms of F_{A0} , X , and $y_{D,e}$. We use the equations for the mole fraction of species D to calculate the conversion at which condensation begins.

TABLE 3-5. STOICHIOMETRIC TABLE FOR REACTION WITH CONDENSATION
 $A(g) + 2B(g) \longrightarrow C(g) + D(g, l)$

Species	Entering	Change	Before Condensation $P_D < P_v$ Leaving	After Condensation $P_D = P_v$ Leaving
A(g)	F_{A0}	$-F_{A0}X$	$F_A = F_{A0}(1 - X)$	$F_{A0}(1 - X)$
B(g)	$F_{B0} = 2F_{A0}$	$-2F_{A0}X$	$F_B = F_{A0}(2 - 2X)$	$F_{A0}(2 - 2X)$
C(g)	—	$F_{A0}X$	$F_C = F_{A0}X$	$F_{A0}X$
D(g)	—	$F_{A0}X$	$F_D = F_{A0}X$ $F_T = F_{A0}(3 - X)$	$F_D = y_{D,e}F_T$ $F_T = y_{D,e}F_T + 3F_{A0} - 2F_{A0}X$

Solve for F_T :
 $F_T = 2F_{A0}(1.5 - X)/(1 - y_{D,e})$

An extra column is added to the table for phase changes

Example 3-10 Expressing $-r_A = g(X)$ for Reactions with Phase Change

For the reaction just discussed, calculate the conversion at which condensation begins and express the concentration of the reacting species and the rate of reaction as a function of conversion. The reaction is first-order in both species A and species B. The feed contains only A and B in stoichiometric amounts and the reaction is carried out isothermally. The total pressure is 101.3 kPa (1 atm) and species D has a vapor pressure of 16 kPa (120 mmHg) at the isothermal reaction temperature of 300 K.

Solution

At the point where condensation begins,

$$X = X_c$$

From the stoichiometric table,

$$y_{D,e} = \frac{F_D}{F_T} = \frac{F_{A0}X_c}{F_{A0}(3 - X_c)} = \frac{X_c}{3 - X_c} \quad (\text{E3-10.1})$$

At saturation,

$$y_{D,e} = \frac{P_{vD}}{P_T} = \frac{16}{101.3} = 0.158 \quad (\text{E3-10.2})$$

$-r_A$ will be a different function of conversion before and after condensation

Equating Equations (E3-10.1) and (E3-10.2) gives

$$0.158 = \frac{X_c}{3 - X_c} \quad (\text{E3-10.3})$$

Solving for X_c yields

$$X_c = 0.41$$

Before condensation begins: For $X < X_c$ there is no condensation and one can use the basic equations for δ and ϵ to calculate the concentrations; i.e.,

$$C_A = \frac{C_{A0}(1 - X)}{1 + \epsilon X} \quad (\text{E3-10.4})$$

$$\epsilon = y_{A0}\delta = 0.33(1 + 1 - 2 - 1) = -0.33$$

$$C_A = C_{A0} \left(\frac{1 - X}{1 - 0.33X} \right) \quad (\text{E3-10.5})$$

$$C_B = C_{A0} \left(\frac{2 - 2X}{1 - 0.33X} \right) = \frac{2C_{A0}(1 - X)}{(1 - 0.33X)} \quad (\text{E3-10.6})$$

Because the temperature and pressure are constant, the total concentration is constant.

$$C_T = \frac{P}{ZRT} = \frac{P_0}{Z_0RT_0} = C_{T0} \quad (\text{E3-10.7})$$

The reaction rate is first-order in A and in B for $X < X_c$:

$$-r_A = 2kC_{A0}^2 \left[\frac{(1 - X)^2}{(1 - 0.33X)^2} \right] \quad (\text{E3-10.8})$$

After condensation begins: For $X > X_c$ the partial pressure of D is equal to the vapor pressure ($P_D = P_v$). The volumetric flow rate is related to the total molar flow rate through the ideal gas equation of state:

$$F_T = C_T v \quad (\text{E3-10.9})$$

$$F_{T0} = C_{T0} v_0 \quad (\text{E3-10.10})$$

Then, taking the ratio of Equation (E3-10.9) to Equation (E3-10.10) and rearranging, we have

$$v = v_0 \left(\frac{F_T}{F_{T0}} \right) = v_0 \left[\frac{2F_{A0}(1.5 - X)}{3F_{A0}(1 - y_{D,e})} \right] = \frac{v_0}{1 - y_{D,e}} \frac{1.5 - X}{1.5} \quad (\text{E3-10.11})$$

We must use the column in the stoichiometric table labeled "after condensation" in conjunction with Equation (E3-10.11) to determine C_A and C_B .

$$C_A = \frac{F_A}{v} = \frac{1.5 F_{A0}(1-X)}{v_0(1.5-X)/(1-y_{D,e})} = 1.5 C_{A0}(1-y_{D,e}) \frac{1-X}{1.5-X} \quad (\text{E3-10.12})$$

$$C_B = \frac{F_B}{v} = \frac{1.5 F_{A0}(2-2X)}{v_0(1.5-X)/(1-y_{D,e})} = 3 C_{A0}(1-y_{D,e}) \frac{1-X}{1.5-X} \quad (\text{E3-10.13})$$

The rate law for $X > X_c$ is

$$-r_A = 4.5 k C_{A0}^2 (1-y_{D,e})^2 \frac{(1-X)^2}{(1.5-X)^2} \quad (\text{E3-10.14})$$

Before condensation, for $X < X_c$, the gas-phase molar flow rate of D is $F_D = F_{A0}X$. After condensation begins (i.e., $X > X_c$), the molar flow rate of D in the gas phase is

$$F_D(g) = y_{D,e} F_T = \frac{y_{D,e}}{1-y_{D,e}} 2F_{A0}(1.5-X) = 0.375 F_{A0}(1.5-X) \quad (\text{E3-10.15})$$

The liquid molar flow rate of D is

$$F_D(l) = F_{A0}X - F_D(g) = F_{A0}(1.375X - 0.563)$$

Plots of the molar flow rates of species D and the total, together with the concentration of A, are shown in Figure E3-10.1 as a function of conversion.

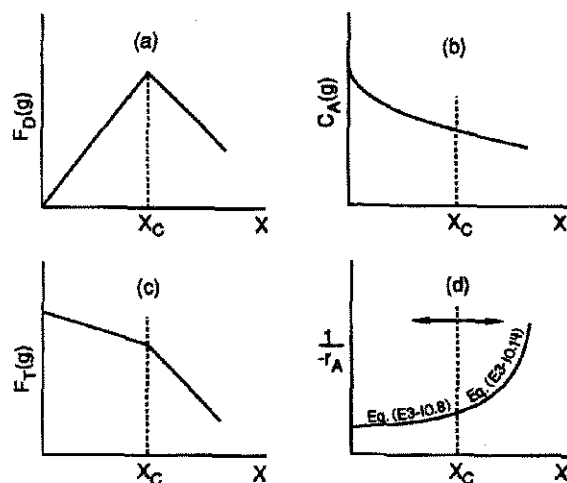


Figure E3-10.1

If we know specific values of v_0 , C_{A0} , and k , we can use Figure E3-10.1(d) to size a variety of combinations of CSTRs and PFRs.

SUMMARY

1. Reaction order is determined from experimental observation:



$$-r_A = k C_A^\alpha C_B^\beta$$

The reaction in Equation (S3-1) is α order with respect to species A and β order with respect to species B, whereas the overall order is $\alpha + \beta$. Reaction order is determined from experimental observation. If $\alpha = 1$ and $\beta = 2$, we would say that the reaction is first-order with respect to A, second-order with respect to B, and overall third-order.

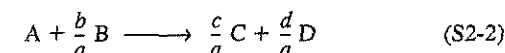
2. In addition to the reaction order, the following terms were defined:

- Elementary reaction
 - Reversible and irreversible reactions
 - Homogeneous and heterogeneous reactions
3. The temperature dependence of a specific reaction rate is given by the Arrhenius equation,

$$k = A e^{-E/RT} \quad (\text{S3-2})$$

where A is the frequency factor and E the activation energy.

4. The stoichiometric table for the reaction



being carried out in a flow system is:

Species	Entering	Change	Leaving
A	F_{A0}	$-F_{A0}X$	$F_{A0}(1-X)$
B	F_{B0}	$-\left(\frac{b}{a}\right) F_{A0}X$	$F_{A0}\left(\Theta_B - \frac{b}{a}X\right)$
C	F_{C0}	$\left(\frac{c}{a}\right) F_{A0}X$	$F_{A0}\left(\Theta_C + \frac{c}{a}X\right)$
D	F_{D0}	$\left(\frac{d}{a}\right) F_{A0}X$	$F_{A0}\left(\Theta_D + \frac{d}{a}X\right)$
I	$\frac{F_{I0}}{F_{T0}}$	—	$\frac{F_{I0}}{F_T = F_{T0} + \delta F_{A0}X}$

where $\delta = \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1$

The relative rates of reaction are

$$\frac{r_A}{-a} = \frac{r_B}{-b} = \frac{r_C}{c} = \frac{r_D}{d} \quad (2-20)$$

5. In the case of ideal gases, Equations (S3-3) through (S3-6) relate volume and volumetric flow rate to conversion.

Batch constant volume: $V = V_0$ (S3-3)

Batch variable volume: $V = V_0 \left(\frac{P_0}{P} \right) (1 + \varepsilon X) \frac{T}{T_0}$ (S3-4)

Flow systems: $v = v_0 \left(\frac{P_0}{P} \right) (1 + \varepsilon X) \frac{T}{T_0}$ (S3-5)

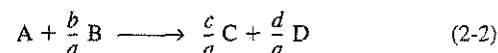
where the change in the number of moles per mole of A fed is

$$\varepsilon = y_{A0} \delta \quad (S3-6)$$

and the change in the number of moles per mole of A reacted is

$$\delta = \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1 \quad (S3-7)$$

6. For the ideal gas-phase reaction



the volumetric flow rate is

$$v = v_0 \left(\frac{F_T}{F_{T0}} \right) \frac{P_0}{P} \left(\frac{T}{T_0} \right) \quad (S3-8)$$

Using the stoichiometric table along with the definitions of concentration (e.g., $C_A = F_A/v$), the concentrations of A and C are:

$$C_A = \frac{F_A}{v} = \frac{F_{A0}(1-X)}{v} = C_{A0} \left[\frac{1-X}{1+\varepsilon X} \right] \frac{P}{P_0} \left(\frac{T_0}{T} \right) \quad (S3-9)$$

$$C_C = \frac{F_C}{v} = C_{A0} \left[\frac{\Theta_C + (c/a)X}{1+\varepsilon X} \right] \frac{P}{P_0} \left(\frac{T_0}{T} \right) \quad (S3-10)$$

7. When the reactants and products are incompressible liquids, the concentrations of species A and C in the reaction given by Equation (2-2) can be written as

$$C_A = C_{A0}(1-X) \quad (S3-11)$$

$$C_C = C_{A0} \left(\Theta_C + \frac{c}{a} X \right) \quad (S3-12)$$

Equations (S3-11) and (S3-12) also hold for gas-phase reactions carried out at constant volume in batch systems.

8. When using measures other than conversion for reactor design, the mole balances are written for each species in the reacting mixture:

$$\frac{dF_A}{dV} = r_A, \quad \frac{dF_B}{dV} = r_B, \quad \frac{dF_C}{dV} = r_C, \quad \frac{dF_D}{dV} = r_D$$

The mole balances are then coupled through their relative rates of reaction. If

$$-r_A = k C_A^\alpha C_B^\beta$$

then

$$r_B = \frac{b}{a} r_A, \quad r_C = -\frac{c}{a} r_A, \quad r_D = -\frac{d}{a} r_A$$

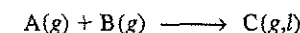
Concentration can also be expressed in terms of the number of moles (batch) in molar flow rates (flow).

Gas: $C_A = C_{T0} \frac{F_A}{F_T} \frac{P}{P_0} \frac{T_0}{T}$ (S3-13)

$$F_T = F_A + F_B + F_C + F_D + F_I$$

Liquid: $C_A = \frac{F_A}{v_0}$ (S3-14)

9. For reactions in which condensation occurs, e.g.,



before condensation, with $P = P_0$, $T = T_0$, $\Theta_B = 1$,

$$v = v_0(1 + \varepsilon X) = v_0(1 - 0.5X) \quad (S3-15)$$

$$C_C = \frac{C_{A0}X}{1 - 0.5X}$$

and after condensation ($X > X_c$),

$$v = \frac{v_0(1-X)}{1-y_{C,e}}, \quad F_C = y_C F_T, \quad y_{C,e} = \frac{P_{vC}}{P_T}, \quad C_C = \frac{y_C}{y_{A0}} C_{A0} \quad (S3-16)$$

where $y_{C,e} = P_{vC}/P_0$ and is the mole fraction of C at which condensation begins.

QUESTIONS AND PROBLEMS

The subscript to each of the problem numbers indicates the level of difficulty: A, least difficult; D, most difficult.

A = ● B = ■ C = ◆ D = ♦♦

In each of the questions and problems below, rather than just drawing a box around your answer, write a sentence or two describing how you solved the problem, the assumptions you made, the reasonableness of your answer, what you learned, and any other facts that you want to include. You may wish to refer to W. Strunk and E. B. White, *The Elements of Style* (New York: Macmillan, 1979) and Joseph M. Williams, *Style: Ten Lessons in Clarity & Grace* (Glenview, Ill.: Scott, Foresman, 1989) to enhance the quality of your sentences.



- P3-1_C** (a) List the important concepts that you learned from this chapter. What concepts are you not clear about?
 (b) Explain the strategy to evaluate reactor design equations and how this chapter expands on Chapter 2.
 (c) Read through all the problems at the end of this chapter. Make up and solve an original problem based on the material in this chapter. (1) Use real data and reactions. (2) Make up your data. Identify what concepts the problem is trying to enforce and why the problem is important. Novel applications (e.g., environmental, food processing) are encouraged. At the end of the problem and solution, describe the process used to generate the idea of the problem. (*Hint:* The journals listed at the end of Chapter 1 may be helpful in obtaining real data.)

P3-2_A What if:

- (a) you were asked to give an example of the material discussed in this chapter that applies to things you observe every day; what would you describe? (*Hint:* See Problem 3-3_A.)
 (b) a catalyst were added to increase the reaction rate by a factor of 10 in Example 3-8? How would your answers change?
 (c) very, very little NaOH were used in Example 3-2 compared to the amount of TBB? Would the rate of reaction be affected? What might be the rate law with respect to TBB?
 (d) a plot of $\ln k$ vs. $(1/T)$ were not linear, but a curve whose slope was shallow at high T and steep at low T or vice versa. How would you explain such curves? (*Hint:* one example $A \rightarrow B$ and $A \rightarrow C$)
 (e) someone suggested that you bake a 9-in.-diameter cake for 15 minutes at 400°F instead of the cookbook's recommendation of 30 minutes at 325°F? How would you develop a plot of cooking time versus oven temperature?

P3-3_A The frequency of flashing of fireflies and the frequency of chirping of crickets as a function of temperature are given below [*J. Chem. Educ.*, 5, 343 (1972) Reprinted by permission.].

For fireflies:

T (°C)	21.0	25.00	30.0
Flashes/min	9.0	12.16	16.2



For crickets:

T (°C)	14.2	20.3	27.0
Chirps/min	80	126	200

The running speed of ants and the flight speed of honeybees as a function of temperature are given below [Source: B. Heinrich, "The Hot-Blooded Insects" (Harvard University Press, Cambridge, MA, 1993)].

For ants:

T (°C)	10	20	30	38
V (cm/s)	0.5	2	3.4	6.5

For honeybees:

T (°C)	25	30	35	40
V (cm/s)	0.7	1.8	3	?

- (a) What do the firefly and cricket have in common?
 (b) What is the velocity of the honeybee at 40°C? At -5°C
 (c) Do the bees, ants, crickets, and fireflies have anything in common? If so, what is it? You may also do a pairwise comparison.
 (d) Would more data help clarify the relationships among frequency, speed, and temperature? If so, in what temperature should the data be obtained? Pick an insect and explain how you would carry out the experiment to obtain more data.

P3-4_B Corrosion of high-nickel stainless steel plates was found to occur in a distillation column used at DuPont to separate HCN and water. Sulfuric acid is always added at the top of the column to prevent polymerization of HCN. Water collects at the bottom of the column and HCN at the top. The amount of corrosion on each tray is shown in Figure P3-4 as a function of plate location in the column.

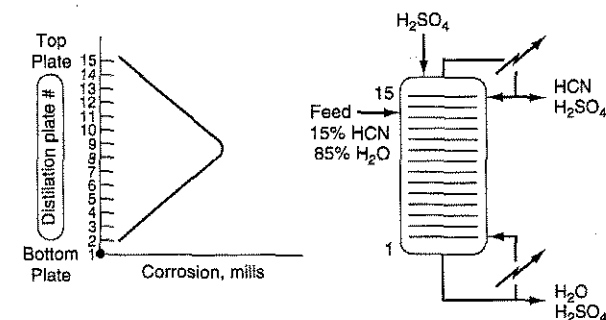


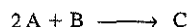
Figure P3-4

The bottom-most temperature of the column is approximately 125°C and the topmost is 100°C. The corrosion rate is a function of temperature and the concentration of a $\text{HCN-H}_2\text{SO}_4$ complex. Suggest an explanation for the observed corrosion plate profile in the column. What effect would the column operating conditions have on the corrosion profile?

- P3-5_B** The rule of thumb that the rate of reaction doubles for a 10°C increase in temperature occurs only at a specific temperature for a given activation energy.
- Develop a relationship between the temperature and activation energy for which the rule of thumb holds. Neglect any variation of concentration with temperature.
 - Determine the activation energy and frequency factor from the following data:

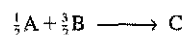
$k \text{ (min}^{-1}\text{)}$	0.001	0.050
$T \text{ (}^\circ\text{C)}$	00.0	100.0

- P3-6_A** In each of the following reactions determine the specific reaction rate constant for each of the other species in the reaction. Assume that k_A in each case has a value of 25 with the appropriate combination of units of mol, dm³, g cat, and s.
- For the reaction



the rate law is $-r_A = k_A C_A^2 C_B$. (Partial ans.: For $k_A = 25 \text{ dm}^6/\text{mol}^2 \cdot \text{s}$, $k_C = k_A/2 = 12.5 \text{ dm}^6/\text{mol}^2 \cdot \text{s}$ and $r_C = 12.5 C_A^2 C_B$.)

- For the reaction



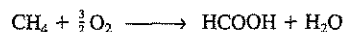
the rate law is $-r_A = k_A C_A C_B$.

- For the solid catalyzed reaction



the rate law is $-r'_A = k_A C_A^2 C_B$ (see Problem 3-13) [$k_D = ?$, $k_B = ?$].

- In the homogeneous gas-phase reaction

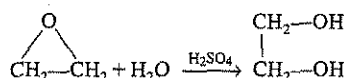


What is the relationship between r_{CH_4} and r_{O_2} ?

- $r_{\text{CH}_4} = r_{\text{O}_2}$
- Cannot tell without the data
- $r_{\text{CH}_4} = \frac{2}{3} r_{\text{O}_2}$
- $r_{\text{CH}_4} = \frac{3}{2} r_{\text{O}_2}$
- None of the above

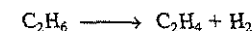
- P3-7_A** Set up a stoichiometric table for each of the following reactions and express the concentration of each species in the reaction as a function of conversion evaluating all constants (e.g., ϵ , Θ).

- The liquid-phase reaction



The initial concentrations of ethylene oxide and water are 1 lb mol/ft³ and 3.47 lb-mol/ft³ (62.41 lb/ft³ ÷ 18), respectively.

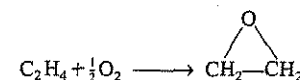
- The isothermal, isobaric gas-phase pyrolysis



Pure ethane enters the flow reactor at 6 atm and 1100 K.

How would your equation for the concentration change if the reaction were to be carried out in a constant-volume batch reactor?

- The isothermal, isobaric, catalytic gas-phase oxidation



The feed enters a PBR at 6 atm and 260°C and is a stoichiometric mixture of oxygen and ethylene.

- P3-8** There were 5430 million pounds of ethylene oxide produced in the United States in 1995. The flowsheet for the commercial production of ethylene oxide (EO) by oxidation of ethylene is shown below. We note that the process essentially consists of two systems, a reaction system and a separation system. Describe how your answers to P3-7 (c) would change if air is used as a feed? This reaction is studied further in *Example 4-6*.

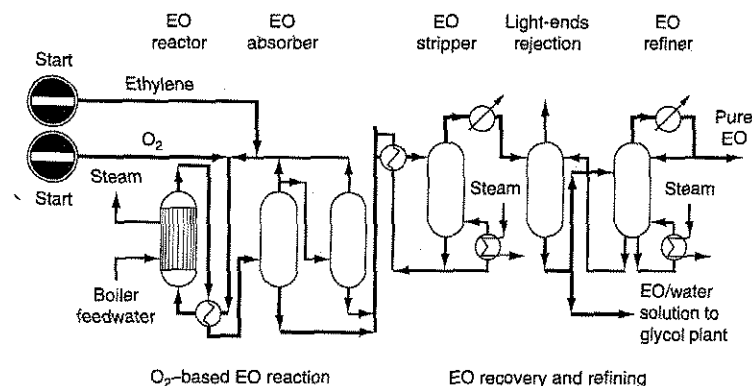


Figure P3-8 EO plant flowsheet. [Adapted from R. A. Meyers, ed., *Handbook of Chemical Production Processes, Chemical Process Technology Handbook Series*, McGraw-Hill, 1983, p. 1.5-5. ISBN 0-67-041-765-2.]

- P3-9** Rework Problem 3-7 to write the combined mole balance rate law along the lines discussed in Section 3.4. Assume each reaction is elementary.
- Write the CSTR mole balance and rate law for each species solely in terms of concentration and rate law parameters for P3-7(a).
 - For Problem 3-7(a) write the combined PFR mole balance on each species and rate law solely in terms of the molar flow rates and rate law parameters.

- (c) For Problem 3-7(b) write the combined PFR mole balance on each species and rate law solely in terms of the molar flow rates and rate law parameters.
- (d) For Problem 3-7(c), write the combined PFR mole balance and rate law solely in terms of the molar flow rates for a PFR.

P3-10_B For each of the following reactions and rate laws at low temperatures, suggest a rate law at high temperatures. The reactions are highly exothermic and therefore reversible at high temperatures.

(a) The reaction



is irreversible at low temperatures, and the rate law is

$$-r_A = kC_A$$

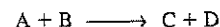
(b) The reaction



is irreversible at low temperatures and the rate law is

$$-r_A = kC_A^{1/2}C_B$$

(c) The catalytic reaction



is irreversible at low temperatures and the rate law is

$$-r'_A = \frac{kP_A P_B}{1 + K_A P_A + K_B P_B}$$

In each case, make sure that the rate laws at high temperatures are thermodynamically consistent at equilibrium (cf. Appendix C).

P3-11_B There were 820 million pounds of phthalic anhydride produced in the United States in 1995. One of the end uses of phthalic anhydride is in the fiberglass of sailboat hulls. Phthalic anhydride can be produced by the partial oxidation of naphthalene in either a fixed or a fluidized catalytic bed. A flowsheet for the commercial process is shown in Figure P3-11. Here the reaction is carried out in a fixed-bed reactor with a vanadium pentoxide catalyst packed in 25-mm-diameter tubes. A production rate of 31,000 tons per year would require 15,000 tubes.

Set up a stoichiometric table for this reaction for an initial mixture of 3.5% naphthalene and 96.5% air (mol %), and use this table to develop the relations listed below. $P_0 = 10$ atm and $T_0 = 500$ K.

- (a) For an isothermal flow reactor in which there is no pressure drop, determine each of the following as a function of the conversion of naphthalene, X_N .
- (1) The partial pressures of O_2 and CO_2 (Ans.: $P_{CO_2} = 0.345 [5.8 - 9/2 X]/(1 - 0.0175 X)$)
 - (2) The concentrations of O_2 and naphthalene (Ans.: $C_N = 0.084 (1 - X)/(1 - 0.0175 X)$)
 - (3) The volumetric flow rate v
- (b) Repeat part (a) when a pressure drop occurs in the reactor.
- (c) If the reaction just happened to be first order in oxygen and second order in naphthalene with a value of k_N of $0.01 \text{ mol}^2/\text{dm}^6 \cdot \text{s}$, write an equation for $-r_N$ solely as a function of conversion for parts (a) and (b).

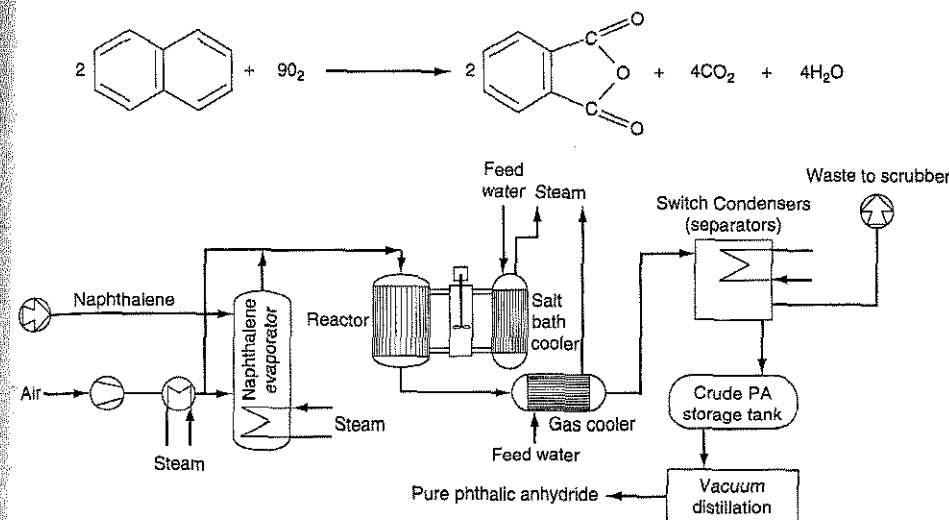
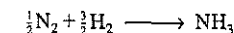


Figure P3-11 [Adapted from *Chemical Engineering, Process Technology and Flowsheet*, Vol. IIK pp. 111 and 125.]

- (d) Rework part (c) for stoichiometric feed of pure oxygen. What would be the advantages and disadvantages of using pure oxygen rather than air?
- (e) What safety features are or should be included in this reaction system? (Hint: See the flowsheet reference.)

[For explosive limits of this reaction, see *Chem. Eng. Prog.*, 66, 49 (1970).]

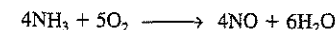
P3-12_A (a) Taking H_2 as your basis of calculation, construct a complete stoichiometric table for the reaction



for an isobaric, isothermal flow system with equimolar feeds of N_2 and H_2 .

- (b) If the entering total pressure is 16.4 atm and the entering temperature is 1727°C , calculate the concentrations of ammonia and hydrogen when the conversion of H_2 is 60%. (Ans.: $C_{H_2} = 0.025 \text{ g mol/L}$, $C_{NH_3} = 0.025 \text{ g mol/L}$.)
- (c) If you took N_2 as your basis of calculation, could 60% conversion of N_2 be achieved?

P3-13_A Nitric acid is made commercially from nitric oxide. Nitric oxide is produced by the gas-phase oxidation of ammonia:



The feed consists of 15 mol % ammonia in air at 8.2 atm and 227°C .

- (a) What is the total entering concentration?
- (b) What is the entering concentration of ammonia?
- (c) Set up a stoichiometric table with ammonia as your basis of calculation.

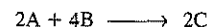
Then

- (1) Express P_i and C_i for all species as functions of conversion for a constant-pressure batch reactor operated isothermally. Express volume as a function of X .
- (2) Express P_i and C_i for all species as functions of conversion for a constant-volume reactor. Express P_T as a function of X .
- (3) Express P_i and C_i for all species as functions of conversion for a flow reactor.
- (d) Referring to Section 3.4, write the combined mole balance and rate law [cf. Equations (E3-9.8 and E3-9.9)] solely in terms of the molar flow rates and rate law parameters. Assume elementary reaction.

P3-14_B Reconsider the decomposition of nitrogen tetroxide discussed in Example 3-8. The reaction is to be carried out in PFR and also in a constant-volume batch reactor at 2 atm and 340 K. Only N_2O_4 and an inert I are to be fed to the reactors. Plot the equilibrium conversion as a function of inert mole fraction in the feed for both a constant-volume batch reactor and a plug flow reactor. Why is the equilibrium conversion lower for the batch system than the flow system in Example 3-8? Will this lower equilibrium conversion result always be the case for batch systems?

- P3-15_A** (a) Express the rate of formation of hydrogen bromide in terms of the constants k_1 and k_2 and the conversion of bromine, X . Evaluate numerically all other quantities. The feed consists of 25% hydrogen, 25% bromine, and 50% inerts at a pressure of 10 atm and a temperature of 400°C.
- (b) Write the rate of decomposition of cumene, $-r'_C$, in terms of conversion, initial concentration of cumene, and the specific rate and equilibrium constants. The initial mixture consists of 75% cumene and 25% inerts.

P3-16_A The gas-phase reaction

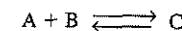


which is first-order in A and first-order in B is to be carried out *isothermally in a plug-flow reactor*. The entering volumetric flow rate is 2.5 dm³/min, and the feed is equimolar in A and B. The entering temperature and pressure are 727°C and 10 atm, respectively. The specific reaction rate at this temperature is 4 dm³/g mol·min and the activation energy is 15,000 cal/g mol.

- (a) What is the volumetric flow rate when the conversion of A is 25%? (Ans.: $v = 1.88$ dm³/min.)
- (b) What is the rate of reaction at the entrance to the reactor (i.e., $X = 0$)? (Ans.: $-r_A = 1.49 \times 10^{-2}$ g mol/dm³·min.)
- (c) What is the rate of reaction when the conversion of A is 40%? (Hint: First express $-r_A$ as a function of X alone.) (Ans.: $-r_A = 4.95 \times 10^{-3}$ g mol/dm³·min.)
- (d) What is the concentration of A at the entrance to the reactor? (Ans.: $C_{A0} = 6.09 \times 10^{-2}$ g mol/dm³.)
- (e) What is the concentration of A at 40% conversion of A? (Ans.: $C_A = 6.09 \times 10^{-2}$ g mol/dm³.)
- (f) What is the value of the specific reaction rate at 1227°C? (Ans.: $k = 49.6$ dm³/g mol·min.)

P3-17_B Calculate the equilibrium conversion and concentrations for each of the following reactions.

- (a) The liquid-phase reaction



with $C_{A0} = C_{B0} = 2$ mol/dm³ and $K_C = 10$ dm³/mol.

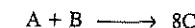
- (b) The gas-phase reaction



carried out in a flow reactor with no pressure drop. Pure A enters at a temperature of 400 K and 10 atm. At this temperature, $K_C = 0.25$ dm³/mol².

- (c) The gas-phase reaction in part (b) carried out in a constant-volume batch reaction.
- (d) The gas-phase reaction in part (b) carried out in a constant-pressure batch reaction.

P3-18_B Consider a *cylindrical batch reactor* that has one end fitted with a frictionless piston attached to a spring (Figure P3-18). The reaction



with the rate expression

$$-r_A = k_1 C_A^2 C_B$$

is taking place in this type of reactor.

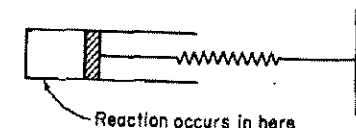


Figure P3-18

- (a) Write the rate law solely as a function of conversion, numerically evaluating all possible symbols. (Ans.: $-r_A = 5.03 \times 10^{-9} [(1-X)^3/(1+3X)^{3/2}]$ lb mol/ft³·s.)
- (b) What is the conversion and rate of reaction when $V = 0.2$ ft³? (Ans.: $X = 0.259$, $-r_A = 8.63 \times 10^{-10}$ lb mol/ft³·s.)

Additional information:

Equal moles of A and B are present at $t = 0$

Initial volume: 0.15 ft³

Value of k_1 : 1.0 (ft³/lb mol)²·s⁻¹

The relationship between the volume of the reactor and pressure within the reactor is

$$V = (0.1)(P) \quad (V \text{ in ft}^3, P \text{ in atm})$$

Temperature of system (considered constant): 140°F

Gas constant: 0.73 ft³·atm/lb mol·°R

- P3-19_C** Find the reaction rate parameters (i.e., reaction order, specific reaction rate at one temperature, and the activation energy) for:
- (a) Three industrial reactions
 - (b) Three laboratory reactions
 - (c) Three reactions discussed in the literature during the last year

- P3-20_C** For families of reactions, the Polanyi-Semenov equation can be used to estimate activation energies from the heats of reaction, ΔH_R according to the equation

$$E = C - \alpha(-\Delta H_R) \quad (\text{P3-20.1})$$

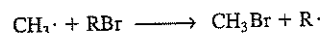
where α and C are constants. For exothermic reactions $\alpha = -0.25$ and $C = 48$ kJ/mol, while for endothermic reactions $\alpha = -0.75$ and $C = 48$ kJ/mol. However, these values may vary somewhat from reaction family to reaction family [K. J. Laidler, *Theories of Chemical Reaction Rates* (New York, R. E. Krieger, 1979), p. 38]. (Also see Appendix J)

- (a) Why is this a reasonable correlation?

Consider the following family of reactions:

	E (kcal/mol)	$-\Delta H_R$ (kcal/mol)
$\text{H} + \text{RBr} \longrightarrow \text{HBr} + \text{R}$	6.8	17.5
$\text{H} + \text{R}'\text{Br} \longrightarrow \text{HBr} + \text{R}'$	6.0	20.0

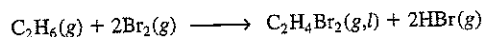
- (b) Estimate the activation energy for the reaction



which has an exothermic heat of reaction of 6 kcal/mol (i.e., $\Delta H_R = -6$ kcal/mol).

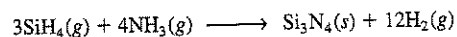
- P3-21_B** The gas-phase reaction between chlorine and methane to form carbon tetrachloride and hydrochloric acid is to be carried out at 75°C and at 950 kPa in a continuous-flow reactor. The vapor pressure of carbon tetrachloride at 75°C is approximately 95 kPa. Set up a stoichiometric table for this reaction with phase change. Calculate the conversion of methane at which *condensation* begins. Plot the concentrations and molar flow rates of each species as well as the total molar flow rate as a function of conversion for a stoichiometric feed. The volumetric flow rate is 0.4 dm³/s.

- P3-22_B** The reaction



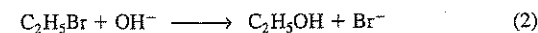
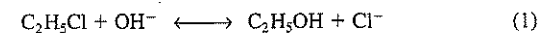
is to be carried out at 200°C and 2500 kPa. The vapor pressure of 1,2-dibromoethane at 200°C is 506.5 kPa. With $k = 0.01$ dm⁶/mol²·min. The reaction is first order in C₂H₆ and second order in Br₂. Calculate the conversion of ethane at which *condensation* begins. Plot the concentration and molar flow rates of each species as well as the total molar flow rate as a function of conversion for a stoichiometric feed. The volumetric flow rate is 0.5 dm³/s. (Ans.: $X_{\text{cond}} = 0.609$.) Are there a set of feed conditions (e.g., equal molar) such that the concentration of C₂H₆(g) will be constant after condensation begins?

- P3-23_B** **Chemical vapor deposition (CVD)** is a process used in the microelectronics industry to deposit thin films of constant thickness on silicon wafers. This process is of particular importance in the manufacturing of very large scale integrated circuits. One of the common coatings is Si₃N₄, which is produced according to the reaction



This dielectric is typically more resistant to oxidation than other coatings. Set up a stoichiometric table for this reaction and plot the concentration of each species as a function of conversion. The entering pressure is 1 Pa and the temperature is constant at 700°C. The feed is equimolar in NH₃ and SiH₄.

- P3-24_B** It is proposed to produce ethanol by one of two reactions:



Use SPARTAN (see Appendix J) or some other software package to answer the following:

- (a) What is the ratio of the rates of reaction at 25°C? 100°C? 500°C?
(b) Which reaction scheme would you choose to make ethanol? (*Hint*: Consult *Chemical Marketing Reporter* or www.chemweek.com for chemical prices).

[Professor R. Baldwin, Colorado School of Mines]



CD-ROM MATERIAL

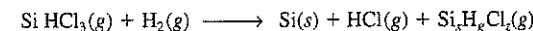
• Learning Resources

1. Summary Notes for Lectures 3 and 4
3. Interactive Computer Modules
 - A. Quiz Show II
4. Solved Problems
 - A. CDP3-A_B Activation Energy for a Beetle Pushing a Ball of Dung.
 - B. CDP3-B_B Microelectronics Industry and the Stoichiometric Table.

- FAQ [Frequently Asked Questions]— In Updates/FAQ icon section
- Additional Homework Problems

CDP3-A_B Estimate how fast a Tenebrionid Beetle can push a ball of dung at 41.5°C. (**Solution included.**)

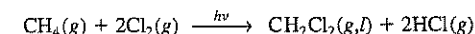
CDP3-B_B Silicon is used in the manufacture of microelectronics devices. Set up a stoichiometric table for the reaction (**Solution included.**)



[2nd Ed. P3-16_B]

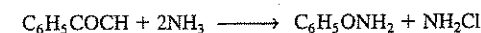
CDP3-C_B The elementary reaction $\text{A}(\text{g}) + \text{B}(\text{g}) \longrightarrow \text{C}(\text{g})$ takes place in a square duct containing liquid B, which evaporates into the gas to react with A. [2nd Ed. P3-20_B]

CDP3-D_B Condensation occurs in the gas phase reaction



[2nd Ed. P3-17_B]

CDP3-E_B Set up a stoichiometric Table for the reaction



[2nd Ed. P3-10_B]

SUPPLEMENTARY READING

1. Two references relating to the discussion of activation energy have already been cited in this chapter. Activation energy is usually discussed in terms of either collision theory or transition-state theory. A concise and readable account of these two theories can be found in

Laidler, K. J. *Chemical Kinetics*. New York: Harper & Row, 1987, Chap. 3.

An expanded but still elementary presentation can be found in

Gardiner, W. C., *Rates and Mechanism of Chemical Reactions*. New York: W. A. Benjamin, 1969, Chaps. 4 and 5.

Moore, J. W., and R. G. Pearson, *Kinetics and Mechanism*, 3rd ed. New York: Wiley, 1981, Chaps. 4 and 5.

A more advanced treatise of activation energies and collision and transition-state theories is

Benson, S. W., *The Foundations of Chemical Kinetics*. New York: McGraw-Hill, 1960.

J. I. Steinfeld, J. S. Francisco, W. L. Hase, *Chemical Kinetics and Dynamics*, Prentice Hall, New Jersey: 1989.

2. The books listed above also give the rate laws and activation energies for a number of reactions; in addition, as mentioned earlier in this chapter, an extensive listing of rate laws and activation energies can be found in NBS circulars:

National Bureau of Standards, *Tables of Chemical Kinetics: Homogeneous Reactions*. Circular 510, Sept. 28, 1951; Supplement 1, Nov. 14, 1956; Supplement 2, Aug. 5, 1960; Supplement 3, Sept. 15, 1961. Washington, D.C.: U.S. Government Printing Office.

3. Also consult the current chemistry literature for the appropriate algebraic form of the rate law for a given reaction. For example, check the *Journal of Physical Chemistry* in addition to the journals listed in Section 4 of the Supplementary Reading section in Chapter 4.

Isothermal 4 Reactor Design

Why, a four-year-old child could understand this.
Someone get me a four-year-old child.

Groucho Marx



In this chapter we bring all the material in the preceding three chapters together to arrive at a logical structure for the design of various types of reactors. By using this structure, one should be able to solve reactor engineering problems through reasoning rather than memorization of numerous equations together with the various restrictions and conditions under which each equation applies (i.e., whether there is a change in the total number of moles, etc.). In perhaps no other area of engineering is mere formula plugging more hazardous; the number of physical situations that can arise appears infinite, and the chances of a simple formula being sufficient for the adequate design of a real reactor are vanishingly small.

This chapter focuses attention on reactors that are operated isothermally. We begin by studying a liquid-phase batch reactor to determine the specific reaction rate constant needed for the design of a CSTR. After illustrating the design of a CSTR from batch reaction rate data, we carry out the design of a tubular reactor for a gas-phase pyrolysis reaction. This is followed by a discussion of pressure drop in packed-bed reactors, equilibrium conversion, and finally, the principles of unsteady operation and semibatch reactors.

4.1 Design Structure for Isothermal Reactors

The following procedure is presented as a pathway for one to follow in the design of isothermal (and in some cases nonisothermal) reactors. It is the author's experience that following this structure, shown in Figure 4-1, will lead to a greater understanding of isothermal reactor design. We begin by applying

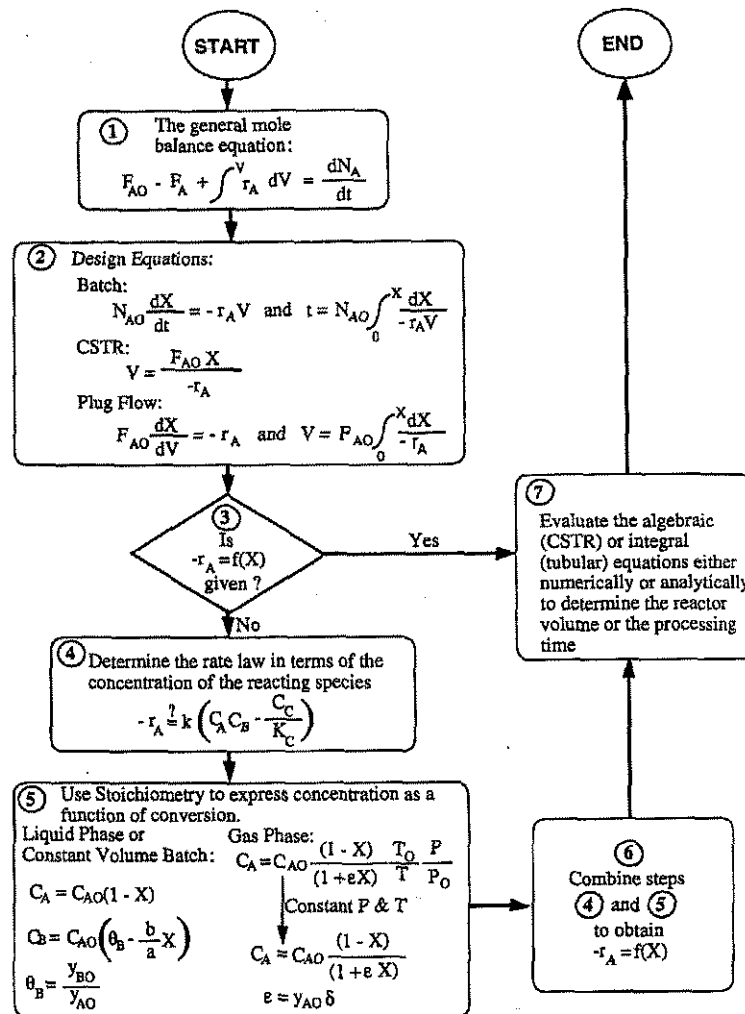


Figure 4-1 Isothermal reaction design algorithm.

our general mole balance equation (level 1) to a specific reactor to arrive at the design equation for that reactor (level 2). If the feed conditions are specified (e.g., N_{AO} or F_{AO}), all that is required to evaluate the design equation is the rate of reaction as a function of conversion at the same conditions as those at which the reactor is to be operated (e.g., temperature and pressure). When $-r_A = f(X)$ is given, one can go directly from level 3 to level 7 to determine either the time or reactor volume necessary to achieve the specified conversion.

If the rate of reaction is not given explicitly as a function of conversion, the rate law must be determined (level 4) by either finding it in books or journals or by determining it experimentally in the laboratory. Techniques for obtaining and analyzing rate data to determine the reaction order and rate constant are presented in Chapter 5. After the rate law has been established, one has only to use stoichiometry (level 5) together with the conditions of the system (e.g., constant volume, temperature) to express concentration as a function of conversion. By combining the information in levels 4 and 5, one can express the rate of reaction as a function of conversion and arrive at level 6. It is now possible to determine either the time or reactor volume necessary to achieve the desired conversion by substituting the relationship relating conversion and rate of reaction into the appropriate design equation. The design equation is then evaluated in the appropriate manner (i.e., analytically using a table of integrals, or numerically using an ODE solver). Although this structure emphasizes the determination of a reaction time or volume for a specified conversion, it can also readily be used for other types of reactor calculations, such as determining the conversion for a specified volume. Different manipulations can be performed in level 7 to answer the types of questions mentioned here.

The structure shown in Figure 4-1 allows one to develop a few basic concepts and then to arrange the parameters (equations) associated with each concept in a variety of ways. Without such a structure, one is faced with the possibility of choosing or perhaps memorizing the correct equation from a multitude of equations that can arise for a variety of different reactions, reactors, and sets of conditions. The challenge is to put everything together in an orderly and logical fashion so that we can proceed to arrive at the correct equation for a given situation.

Fortunately, by using an algorithm to formulate CRE problems, which happens to be analogous to ordering dinner from a fixed-price menu in a fine French restaurant, we can eliminate virtually all memorization. In both of these algorithms we must make choices in each category. For example, in ordering from a French menu, we begin by choosing one dish from the *appetizers* listed. Step 1 in the analog in CRE is to begin by choosing the mole balance for one of the three types of reactors shown. In step 2 we choose the rate law (*entrée*), and in step 3 we specify whether the reaction is gas or liquid phase (*cheese* or *dessert*). Finally, in step 4 we combine steps 1, 2, and 3 and obtain an analytical solution or solve the equations using an ordinary differential equation (ODE) solver. (See complete French menu on the CD-ROM)

We now will apply this algorithm to a specific situation. The first step is to derive or apply the mole balance equation for the system at hand. Suppose that we have, as shown in Figure 4-2, mole balances for three reactors, three

Use the algorithm
rather than
memorizing
equations

French
Menu
Analogy

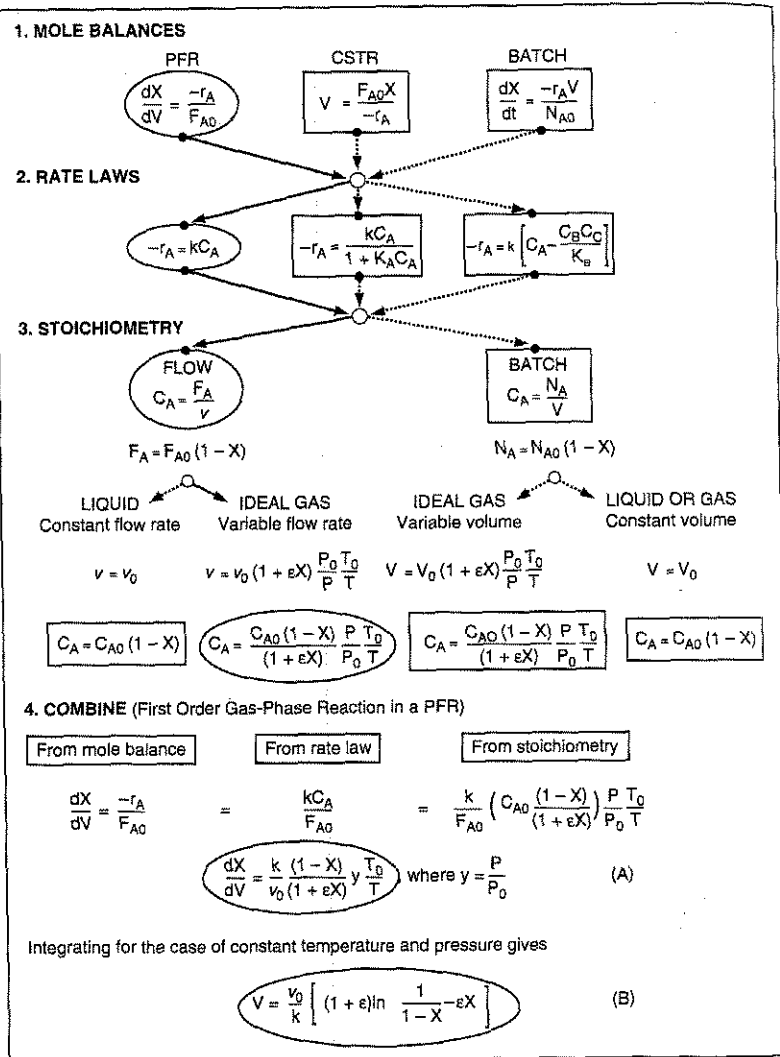


Figure 4-2 Algorithm for isothermal reactors.

rate laws, and the equations for concentrations for both liquid and gas phases. In Figure 4-2 the algorithm is used to formulate the equation to calculate the PFR reactor volume for a first-order gas-phase reaction and the pathway to arrive at this equation is shown by the ovals connected to the dark lines through the algorithm. The dashed lines and the boxes represent other pathways for solutions to other situations. For the reactor and reaction specified we will choose

1. the mole balance on species A for a PFR,
2. the rate law for an irreversible first-order reaction,
3. the equation for the concentration of species A in the gas phase (stoichiometry), and then
4. combine to calculate the volume necessary to achieve a given conversion or calculate the conversion that can be achieved in a specified reaction volume.

For the case of isothermal operation with no pressure drop, we were able to obtain an analytical solution, given by equation B, which gives the reactor volume necessary to achieve a conversion X for a gas-phase reaction carried out isothermally in a PFR. However, in the majority of situations, analytical solutions to the ordinary differential equations appearing in the combine step are not possible. Consequently, we include POLYMATH, or some other ODE solver such as MATLAB, in our menu in that it makes obtaining solutions to the differential equations much more palatable.

4.2 Scale-Up of Liquid-Phase Batch Reactor Data to the Design of a CSTR

One of the jobs in which chemical engineers are involved is the scale-up of laboratory experiments to pilot-plant operation or to full-scale production. In the past, a pilot plant would be designed based on laboratory data. However, owing to the high cost of a pilot-plant study, this step is beginning to be surpassed in many instances by designing a full-scale plant from the operation of a laboratory-bench-scale unit called a *microplant*. To make this jump successfully requires a thorough understanding of the chemical kinetics and transport limitations. In this section we show how to analyze a laboratory-scale batch reactor in which a liquid-phase reaction of known order is being carried out. After determining the specific reaction rate, k , from a batch experiment, we use it in the design of a full-scale flow reactor.

4.2.1 Batch Operation

In modeling a batch reactor, we have assumed that there is no inflow or outflow of material and that the reactor is well mixed. For most liquid-phase reactions, the density change with reaction is usually small and can be neglected (i.e., $V = V_0$). In addition, for gas phases in which the batch reactor

volume remains constant, we also have $V = V_0$. Consequently, for constant-volume ($V = V_0$) (e.g., closed metal vessels) batch reactors the mole balance

$$\frac{1}{V} \left(\frac{dN_A}{dt} \right) = r_A \quad (4-1)$$

can be written in terms of concentration.

$$\frac{1}{V} \frac{dN_A}{dt} = \frac{1}{V_0} \frac{dN_A}{dt} = \frac{d(N_A/V_0)}{dt} = \frac{dC_A}{dt} = r_A \quad (4-2)$$

Generally, when analyzing laboratory experiments it is best to process the data in terms of the measured variable. Since concentration is the measured variable for most liquid-phase reactions, the general mole balance equation applied to reactions in which there is no volume change becomes

$$\text{Mole balance} \quad -\frac{dC_A}{dt} = -r_A$$

We consider the reaction



which is irreversible and second order in A. The rate at which A is being consumed is given by the rate law

$$\text{Rate law} \quad -r_A = kC_A^2 \quad (4-3)$$

We combine the rate law and the mole balance to obtain

$$\begin{aligned} -\frac{dC_A}{dt} &= kC_A^2 \\ -\frac{dC_A}{kC_A^2} &= dt \end{aligned} \quad (4-4)$$

Initially, $C_A = C_{A0}$ at $t = 0$. If the reaction is carried out isothermally, we can integrate this equation to obtain the reactant concentration at any time t :

$$\begin{aligned} \frac{-1}{k} \int_{C_{A0}}^{C_A} \frac{dC_A}{C_A^2} &= \int_0^t dt \\ \frac{1}{k} \left(\frac{1}{C_A} - \frac{1}{C_{A0}} \right) &= t \end{aligned} \quad (4-5)$$

Second-order,
isothermal,
liquid-phase
batch reaction

This time is the time t needed to reduce the reactant concentration in a batch reactor from an initial value C_{A0} to some specified value C_A .

The total cycle time in any batch operation is considerably longer than the reaction time, t_R , as one must account for the time necessary to fill (t_f) and empty (t_e) the reactor together with the time necessary to clean the reactor between batches, t_c . In some cases the reaction time calculated from Equation (4-5) may be only a small fraction of the total cycle time, t_t .

$$t_t = t_f + t_e + t_c + t_R$$

Typical cycle times for a batch polymerization process are shown in Table 4-1. Batch polymerization reaction times may vary between 5 and 60 h. Clearly, decreasing the reaction time with a 60-h reaction is a critical problem. As the reaction time is reduced, it becomes important to use large lines and pumps to achieve rapid transfers and to utilize efficient sequencing to minimize the cycle time.

TABLE 4-1. TYPICAL CYCLE TIMES FOR A BATCH POLYMERIZATION PROCESS

Activity	Time (h)
1. Charge feed to the reactor and agitate, t_f	1.5–3.0
2. Heat to reaction temperature, t_e	1.0–2.0
3. Carry out reaction, t_R	(varies)
4. Empty and clean reactor, t_c	0.5–1.0
Total time excluding reaction	3.0–6.0

Batch operation
times

It is important to have a grasp of the order of magnitude of batch reaction times, t_R , in Table 4-1 to achieve a given conversion, say 90%, for the different values of the specific reaction rate, k . We can obtain these estimates by considering the irreversible reaction



carried out in a constant-volume batch reactor for a first- and a second-order reaction. We start with a mole balance and then follow our algorithm as shown in Table 4-2.

TABLE 4-2. ALGORITHM TO ESTIMATE REACTION TIMES

Mole balance	$\frac{dX}{dt} = \frac{-r_A}{N_{A0}} V$	
Rate law	First-order $-r_A = kC_A$	Second-order $-r_A = kC_A^2$
Stoichiometry ($V = V_0$)	$C_A = \frac{N_A}{V_0} = C_{A0}(1 - X)$	
Combine	$\frac{dX}{dt} = k(1 - X)$	$\frac{dX}{dt} = kC_{A0}(1 - X)^2$
Integrate	$t = \frac{1}{k} \ln \frac{1}{1 - X}$	$t = \frac{X}{kC_{A0}(1 - X)}$

For first-order reactions the reaction time to reach 90% conversion (i.e., $X = 0.9$) in a constant-volume batch reactor scales as

$$t_R = \frac{1}{k} \ln \frac{1}{1-X} = \frac{1}{k} \ln \frac{1}{1-0.9} = \frac{2.3}{k}$$

If $k = 10^{-4} \text{ s}^{-1}$,

$$t_R = \frac{2.3}{10^{-4} \text{ s}^{-1}} = 23,000 \text{ s} = 6.4 \text{ h}$$

The time necessary to achieve 90% conversion in a batch reactor for an irreversible first-order reaction in which the specific reaction rate is 10^{-4} s^{-1} is 6.4 h.

For second-order reactions, we have

$$t_R = \frac{1}{kC_{A0}} \frac{X}{1-X} = \frac{0.9}{kC_{A0}(1-0.9)} = \frac{9}{kC_{A0}}$$

If $kC_{A0} = 10^{-3} \text{ s}^{-1}$,

$$t_R = \frac{9}{10^{-3} \text{ s}^{-1}} = 9000 \text{ s} = 2.5 \text{ h}$$

Table 4-3 gives the *order of magnitude* of time to achieve 90% conversion for first- and second-order irreversible batch reactions.



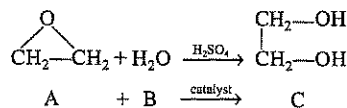
Estimating Reaction Times

TABLE 4-3. BATCH REACTION TIMES

Reaction Time t_R	First-Order $k \text{ (s}^{-1}\text{)}$	Second-Order $kC_{A0} \text{ (s}^{-1}\text{)}$
Hours	10^{-4}	10^{-3}
Minutes	10^{-2}	10^{-1}
Seconds	1	10
Milliseconds	1000	10,000

Example 4-1 Determining k from Batch Data

It is desired to design a CSTR to produce 200 million pounds of ethylene glycol per year by hydrolyzing ethylene oxide. However, before the design can be carried out, it is necessary to perform and analyze a batch reactor experiment to determine the specific reaction rate constant. Since the reaction will be carried out isothermally, the specific reaction rate will need to be determined only at the reaction temperature of the CSTR. At high temperatures there is a significant by-product formation, while at temperatures below 40°C the reaction does not proceed at a significant rate; consequently, a temperature of 55°C has been chosen. Since the water is usually present in excess, its concentration may be considered constant during the course of the reaction. The reaction is first-order in ethylene oxide.



In the laboratory experiment, 500 mL of a 2 M solution (2 kmol/m^3) of ethylene oxide in water was mixed with 500 mL of water containing 0.9 wt % sulfuric acid, which is a catalyst. The temperature was maintained at 55°C . The concentration of ethylene glycol was recorded as a function of time (Table E4-1.1). From these data, determine the specific reaction rate at 55°C .

TABLE E4-1.1. CONCENTRATION-TIME DATA

Time (min)	Concentration of Ethylene Glycol (kmol/m^3) ^a
0.0	0.000
0.5	0.145
1.0	0.270
1.5	0.376
2.0	0.467
3.0	0.610
4.0	0.715
6.0	0.848
10.0	0.957

^a $1 \text{ kmol/m}^3 = 1 \text{ mol/dm}^3 = 1 \text{ mol/L}$.

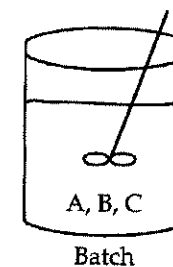
Check 10 types of homework problems on the CD-ROM for more solved examples using this algorithm.



In this example we use the problem-solving algorithm (A through G) that is given in the CD-ROM and on the web "<http://www.engin.umich.edu/~problemsolving>". You may wish to follow this algorithm in solving the other examples in this chapter and the problems given at the end of the chapter. However, to conserve space it will not be repeated for other example problems.

A. *Problem statement.* Determine the specific reaction rate, k_A .

B. *Sketch:*



C. *Identify:*

C1. Relevant theories

$$\text{Rate law: } -r_A = k_A C_A$$

$$\text{Mole balance: } \frac{dN_A}{dt} = r_A V$$

C2. Variables

Dependent: concentrations

Independent: time

C3. Knowns and unknowns

Knowns: concentration of ethylene glycol as a function of time

Unknowns:

1. Concentration of ethylene oxide as a function of time
2. Specific reaction rate
3. Reactor volume

C4. Inputs and outputs: reactant fed all at once to a batch reactor

C5. Missing information: None; does not appear that other sources need to be sought.

D. Assumptions and approximations:

Assumptions

1. Well mixed
2. All reactants enter at the same time
3. No side reactions
4. Negligible filling and emptying time
5. Isothermal operation

Approximations

1. Water in excess so that its concentration is essentially constant.

E. *Specification.* The problem is neither overspecified nor underspecified.F. *Related material.* This problem uses the mole balances developed in Chapter 1 for a batch reactor and the stoichiometry and rate laws developed in Chapter 3.G. *Use an algorithm.* For an isothermal reaction, use the chemical reaction engineering algorithm shown in Figure 4-2.

Solution

1. A **mole balance** on a batch reactor that is well mixed is

$$\frac{1}{V} \frac{dN_A}{dt} = r_A \quad (\text{E4-1.1})$$

2. The **rate law** is

$$-r_A = kC_A \quad (\text{E4-1.2})$$

Since water is present in such excess, the concentration of water at any time t is virtually the same as the initial concentration and the rate law is independent of the concentration of H_2O . ($C_B \approx C_{B0}$.)

3. **Stoichiometry.** Liquid phase, no volume change, $V = V_0$ (Table E4-1.2):

TABLE E4-1.2. STOICHIOMETRIC TABLE

Species	Symbol	Initial	Change	Remaining	Concentration
$\text{CH}_2\text{CH}_2\text{O}$	A	N_{A0}	$-N_{A0}X$	$N_A = N_{A0}(1 - X)$	$C_A = C_{A0}(1 - X)$
H_2O	B	$\Theta_B N_{A0}$	$-N_{A0}X$	$N_B = N_{A0}(\Theta_B - X)$	$C_B = C_{A0}(\Theta_B - X)$
					$C_B \approx C_{A0}\Theta_B = C_{B0}$
$(\text{CH}_2\text{OH})_2$	C	0	$N_{A0}X$	$N_C = N_{A0}X$	$C_C = C_{A0}X$
		N_{T0}		$N_T = N_{T0} - N_{A0}X$	

$$C_A = \frac{N_A}{V} = \frac{N_A}{V_0}$$

$$\frac{1}{V_0} \left(\frac{dN_A}{dt} \right) = \frac{d(N_A/V_0)}{dt} = \frac{dC_A}{dt}$$

4. **Combining** the rate law and the mole balance, we have

$$-\frac{dC_A}{dt} = kC_A \quad (\text{E4-1.3})$$

For isothermal operation we can integrate this equation,

$$-\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A} = \int_0^t k dt$$

using the initial condition that when $t = 0$, then $C_A = C_{A0}$. The initial concentration of A after mixing the two volumes together is 1.0 kmol/m^3 (1 mol/L).

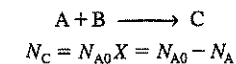
5. **Integrating** yields

$$\ln \frac{C_{A0}}{C_A} = kt \quad (\text{E4-1.4})$$

The concentration of ethylene oxide at any time t is

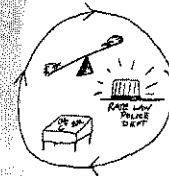
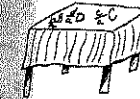
$$C_A = C_{A0}e^{-kt} \quad (\text{E4-1.5})$$

The concentration of ethylene glycol at any time t can be obtained from the reaction stoichiometry:

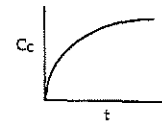
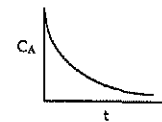
For liquid-phase reactions $V = V_0$,

$$C_C = \frac{N_C}{V} = \frac{N_C}{V_0} = C_{A0} - C_A = C_{A0}(1 - e^{-kt}) \quad (\text{E4-1.6})$$

Stoichiometric table for constant volume



Combining mole balance, rate law, and stoichiometry



Following the algorithm



Rate Law

Rearranging and taking the logarithm of both sides yields

$$\ln \frac{C_{A0} - C_C}{C_{A0}} = -kt \quad (\text{E4-1.7})$$

We see that a plot of $\ln[(C_{A0} - C_C)/C_{A0}]$ as a function of t will be a straight line with a slope $-k$. Calculating the quantity $(C_{A0} - C_C)/C_{A0}$ (Table E4-1.3) and then plot-

TABLE E4-1.3

t (min)	C_C (kmol/m ³)	$\frac{C_{A0} - C_C}{C_{A0}}$
0.0	0.000	1.000
0.5	0.145	0.855
1.0	0.270	0.730
1.5	0.376	0.624
2.0	0.467	0.533
3.0	0.610	0.390
4.0	0.715	0.285
6.0	0.848	0.152
10.0	0.957	0.043

ting $(C_{A0} - C_C)/C_{A0}$ versus t on semilogarithmic paper is shown in Figure E4-1.1. The slope of this plot is also equal to $-k$. Using the decade method (see Appendix D) between $(C_{A0} - C_C)/C_{A0} = 0.6$ ($t = 1.55$ min) and $(C_{A0} - C_C)/C_{A0} = 0.06$ ($t = 8.95$ min) to evaluate the slope

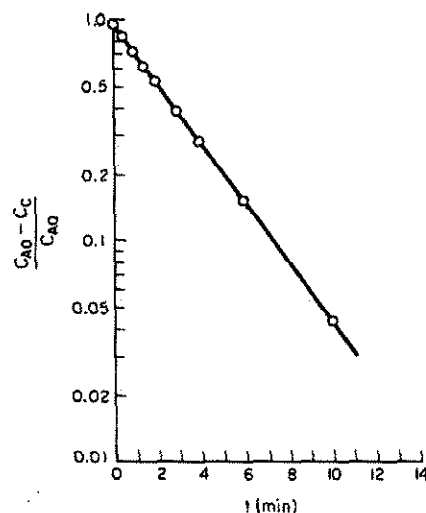


Figure E4-1.1

Evaluating the
specific reaction
rate from
batch reactor
concentration-time
data

$$k = \frac{\ln 10}{t_2 - t_1} = \frac{2.3}{8.95 - 1.55} = 0.311 \text{ min}^{-1} \quad (\text{E4-1.8})$$

the rate law becomes

$$-r_A = (0.311 \text{ min}^{-1})C_A \quad (\text{E4-1.9})$$

This rate law can now be used in the design of an industrial CSTR.

4.2.2 Design of CSTRs

In Chapter 2 we derived the following design equation for a CSTR:

$$\text{Mole balance} \quad V = \frac{F_{A0}X}{(-r_A)_{\text{exit}}} \quad (2-13)$$

which gives the volume V necessary to achieve a conversion X . When the volumetric flow rate does not change with reaction, (i.e., $v = v_0$) we can write

$$V = v_0 \left(\frac{C_{A0} - C_A}{-r_A} \right) \quad (4-6)$$

or in terms of the space time,

$$\tau = \frac{V}{v_0} = \frac{C_{A0} - C_A}{-r_A} \quad (4-7)$$

For a first-order irreversible reaction, the rate law is

$$\text{Rate law} \quad -r_A = kC_A$$

We can combine the rate law and mole balance to give

$$\text{Combine} \quad \tau = \frac{C_{A0} - C_A}{kC_A}$$

Solving for the effluent concentration of A, C_A , we obtain

$$C_A = \frac{C_{A0}}{1 + \tau k} \quad (4-8)$$

For the case we are considering, there is no volume change during the course of the reaction, so we can use Equation (3-29),

$$C_A = C_{A0}(1 - X) \quad (3-29)$$

to combine with Equation (4-8) to give

$$X = \frac{\tau k}{1 + \tau k} \quad (4-9)$$

Relationship
between space time
and conversion for a
first-order liquid-
phase reaction

$$Da = \frac{-r_{A0}V}{F_{A0}}$$

For a first-order reaction the product τk is often referred to as the reaction **Damköhler number**.

The Damköhler is a dimensionless number that can give us a quick estimate of the degree of conversion that can be achieved in continuous-flow reactions. The Damköhler number is the ratio of the rate of reaction of A to the rate of convective transport of A at the entrance to the reactor. For first- and second-order irreversible reactions the Damköhler numbers are

$$Da = \frac{-r_{A0}V}{F_{A0}} = \frac{kC_{A0}V}{v_0C_{A0}} = \tau k$$

and

$$Da = \frac{kC_{A0}^2V}{v_0C_{A0}} = \tau k C_{A0}$$

respectively. It is important to know what values of the Damköhler number, Da , give high and low conversion in continuous-flow reactors. A value of $Da = 0.1$ or less will usually give less than 10% conversion and a value of $Da = 10.0$ or greater will usually give greater than 90% conversion.

$$0.1 < Da < 10$$

CSTRs in Series. A first-order reaction with no volume change ($v = v_0$) is to be carried out in two CSTRs placed in series (Figure 4-3). The effluent con-

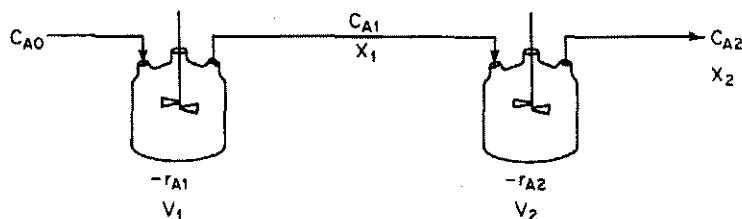


Figure 4-3 Two CSTRs in series.

centration of A from reactor 1 is

$$C_{A1} = \frac{C_{A0}}{1 + \tau_1 k_1}$$

From a mole balance on reactor 2,

$$V_2 = \frac{F_{A1} - F_{A2}}{-r_{A2}} = \frac{v_0(C_{A1} - C_{A2})}{k_2 C_{A2}}$$

Solving for C_{A2} , the concentration exiting the second reactor, we get

1st order reaction

$$C_{A2} = \frac{C_{A1}}{1 + \tau_2 k_2} = \frac{C_{A0}}{(1 + \tau_2 k_2)(1 + \tau_1 k_1)}$$

If instead of two CSTRs in series we had n equal-sized CSTRs connected in series ($\tau_1 = \tau_2 = \dots = \tau_n = \tau$) operating at the same temperature ($k_1 = k_2 = \dots = k_n = k$), the concentration leaving the last reactor would be

$$C_{A_n} = \frac{C_{A0}}{(1 + \tau k)^n} = \frac{C_{A0}}{(1 + Da)^n} \quad (4-10)$$

The conversion for these n tank reactors in series would be

Conversion as a function of the number of tanks in series

$$X = 1 - \frac{1}{(1 + \tau k)^n} \quad (4-11)$$

A plot of the conversion as a function of the number of reactors in series for a first-order reaction is shown in Figure 4-4 for various values of the Damköhler

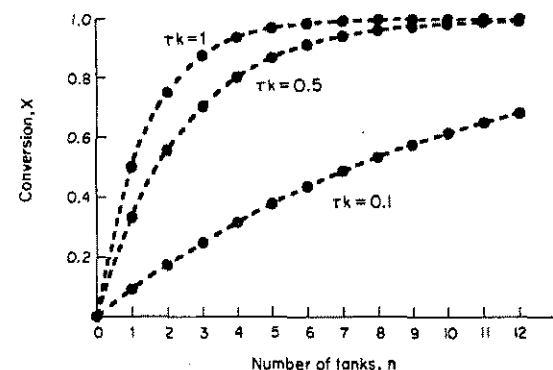


Figure 4-4 Conversion as a function of the number of tanks in series for different Damköhler numbers for a first-order reaction.

number τk . Observe from Figure 4-4 that when the product of the space time and the specific reaction rate is relatively large, say, $Da \geq 1$, approximately 90% conversion is achieved in two or three reactors; thus the cost of adding subsequent reactors might not be justified. When the product τk is small, $Da \sim 0.1$, the conversion continues to increase significantly with each reactor added.

The rate of disappearance of A in the n th reactor is

$$-r_{A_n} = kC_{A_n} = k \frac{C_{A0}}{(1 + \tau k)^n}$$

CSTRs in Parallel. We now consider the case in which equal-sized reactors are placed in parallel rather than in series, and the feed is distributed equally among each of the reactors (Figure 4-5). A balance on any reactor, say i , gives

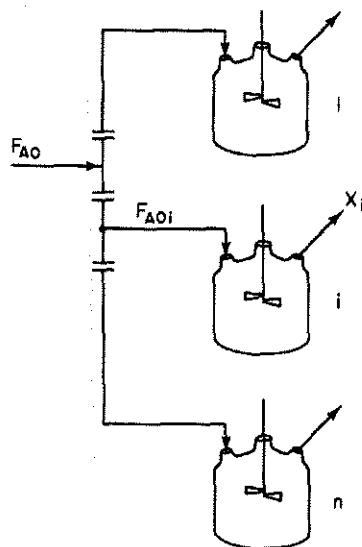


Figure 4-5 CSTRs in parallel.

the individual reactor volume

$$V_i = F_{A0i} \left(\frac{X_i}{-r_{Ai}} \right) \quad (4-12)$$

Since the reactors are of equal size, operate at the same temperature, and have identical feed rates, the conversion will be the same for each reaction:

$$X_1 = X_2 = \dots = X_n = X$$

as will be the rate of reaction in each reactor

$$-r_{A1} = -r_{A2} = \dots = -r_{An} = -r_A$$

The volume of each individual reactor, V_i , is related to the total volume, V , of all the reactors by the equation

$$V_i = \frac{V}{n}$$

A similar relationship exists for the total molar flow rate:

$$F_{A0i} = \frac{F_{A0}}{n}$$

Substituting these values into Equation (4-12) yields

$$\frac{V}{n} = \frac{F_{A0}}{n} \left(\frac{X_i}{-r_{Ai}} \right)$$

or

Conversion for
tanks in parallel

$$V = \frac{F_{A0} X_i}{-r_{Ai}} = \frac{F_{A0} X}{-r_A} \quad (4-13)$$

This result shows that the conversion achieved in any one of the reactors in parallel is identical to what would be achieved if the reactant were fed in one stream to one large reactor of volume V !

A Second-Order Reaction in a CSTR. For a second-order liquid-phase reaction being carried out in a CSTR, the combination of the rate law and the design equation yields

$$V = \frac{F_{A0} X}{k C_A^2} \quad (4-14)$$

For constant density $v = v_0$, $F_{A0} X = v_0 (C_{A0} - C_A)$, then

$$\tau = \frac{V}{v_0} = \frac{C_{A0} - C_A}{k C_A^2}$$

Using our definition of conversion, we have

$$\tau = \frac{X}{k C_{A0} (1 - X)^2} \quad (4-15)$$

We solve Equation (4-15) for the conversion X :

$$\begin{aligned} X &= \frac{(1 + 2\tau k C_{A0}) - \sqrt{(1 + 2\tau k C_{A0})^2 - (2\tau k C_{A0})^2}}{2\tau k C_{A0}} \\ &= \frac{(1 + 2\tau k C_{A0}) - \sqrt{1 + 4\tau k C_{A0}}}{2\tau k C_{A0}} \\ &= \frac{(1 + 2Da) - \sqrt{1 + 4Da}}{2Da} \end{aligned} \quad (4-16)$$

Conversion for
a second-order
liquid-phase
reaction
in a CSTR

The minus sign must be chosen in the quadratic equation because X cannot be greater than 1. Conversion is plotted as a function of the Damköhler parameter, $\tau k C_{A0}$, in Figure 4-6. Observe from this figure that at high conver-

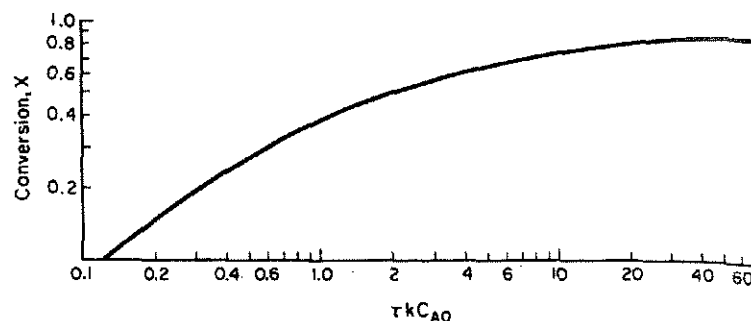


Figure 4-6 Conversion as a function of the Damköhler number ($\tau k C_{A0}$) for a second order reaction in a CSTR.

sions (say 70%) a 10-fold increase in the reactor volume (or increase in the specific reaction rate by raising the temperature) will increase the conversion only to 85%. This is a consequence of the fact that the CSTR operates under the condition of the lowest value of the reactant concentration (i.e., the exit concentration), and consequently the smallest value of the rate of reaction.

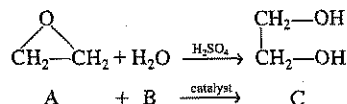
Example 4-2 Producing 200 Million Pounds per Year in a CSTR

Close to 5.2 billion pounds of ethylene glycol were produced in 1995, which ranked it the twenty-sixth most produced chemical in the nation that year on a total pound basis. About one-half of the ethylene glycol is used for *antifreeze* while the other half is used in the manufacture of polyesters. In the polyester category, 88% was used for fibers and 12% for the manufacture of bottles and films. The 1997 selling price for ethylene glycol was \$0.38 per pound.

It is desired to produce 200 million pounds per year of ethylene glycol. The reactor is to be operated isothermally. A 1 lb mol/ft³ solution of ethylene oxide in water is fed to the reactor together with an equal volumetric solution of water containing 0.9 wt % of the catalyst H₂SO₄. If 80% conversion is to be achieved, determine the necessary reactor volume. How many 800-gal reactors would be required if they are arranged in parallel? What is the corresponding conversion? How many 800-gal reactors would be required if they are arranged in series? What is the corresponding conversion? The specific reaction rate constant is 0.311 min⁻¹, as determined in Example 4-1.

Solution

Assumption: Ethylene glycol is the only reaction product formed.



Uses and economics



The specified production rate in lb mol/min is

$$F_C = 2 \times 10^8 \frac{\text{lb}}{\text{yr}} \times \frac{1 \text{ yr}}{365 \text{ days}} \times \frac{1 \text{ day}}{24 \text{ h}} \times \frac{1 \text{ h}}{60 \text{ min}} \times \frac{1 \text{ lb mol}}{62 \text{ lb}} = 6.137 \frac{\text{lb mol}}{\text{min}}$$

From the reaction stoichiometry

$$F_C = F_{A0} X$$

we find the required molar flow rate of ethylene oxide to be

$$F_{A0} = \frac{F_C}{X} = \frac{6.137}{0.8} = 7.67 \frac{\text{lb mol}}{\text{min}} \quad (58.0 \text{ g mol/s})$$

We can now calculate the reactor volume using the following equations:

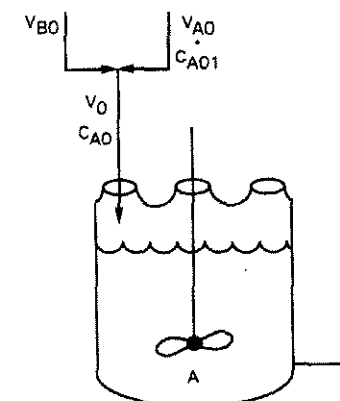


Figure E4-2.1 Single CSTR.

Following the algorithm

1. Design equation:

$$V = \frac{F_{A0} X}{-r_A} \quad (\text{E4-2.1})$$

2. Rate law:

$$-r_A = k C_A \quad (\text{E4-2.2})$$

3. Stoichiometry. Liquid phase ($v = v_0$):

$$C_A = C_{A0}(1 - X) \quad (\text{E4-2.3})$$

4. Combining:

$$V = \frac{F_{A0} X}{k C_{A0}(1 - X)} = \frac{v_0 X}{k(1 - X)} \quad (\text{E4-2.4})$$

The entering volumetric flow rate of stream A, with $C_{A01} = 1 \frac{\text{mol}}{\text{dm}^3}$ before mixing, is

$$v_{A0} = \frac{F_{A0}}{C_{A01}} = \frac{7.67 \text{ lb mol/min}}{1 \text{ lb mol/ft}^3} = 7.67 \frac{\text{ft}^3}{\text{min}}$$

From the problem statement

$$v_{B0} = v_{A0}$$

The total entering volumetric flow rate of liquid is

$$v_0 = v_{A0} + v_{B0} = 15.34 \frac{\text{ft}^3}{\text{min}} \quad (7.24 \text{ dm}^3/\text{s})$$

5. **Substituting** in Equation (E4-2.4), recalling that $k = 0.311 \text{ min}^{-1}$, yields

$$V = \frac{v_0 X}{k(1-X)} = 15.34 \frac{\text{ft}^3}{\text{min}} \frac{0.8}{(0.311 \text{ min}^{-1})(1-0.8)} = 197.3 \text{ ft}^3 \\ = 1480 \text{ gal} \quad (5.6 \text{ m}^3)$$

A tank 5 ft in diameter and approximately 10 ft tall is necessary to achieve 80% conversion.

6. **CSTRs in parallel.** For two 800-gal CSTRs arranged in parallel with $7.67 \text{ ft}^3/\text{min}$ ($v_0/2$) fed to each reactor, the conversion achieved can be calculated from

$$X = \frac{\tau k}{1 + \tau k} \quad (\text{E4-2.5})$$

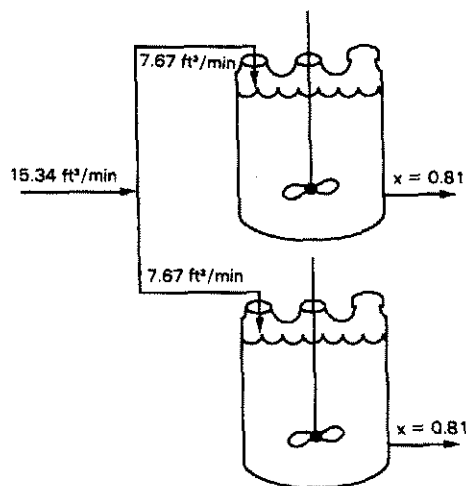


Figure E4-2.2 CSTRs in parallel.

where

$$\tau = \frac{V}{v_0/2} = \left(800 \text{ gal} \times \frac{1 \text{ ft}^3}{7.48 \text{ gal}} \right) \times \frac{1}{7.67 \text{ ft}^3/\text{min}} = 13.94 \text{ min}$$

The **Damköhler number** is

$$\text{Da} = \tau k = 13.94 \text{ min} \times \frac{0.311}{\text{min}} = 4.34$$

Substituting into Equation (E4-2.5) gives us

$$X = \frac{4.34}{1 + 4.34} = 0.81$$

7. **CSTRs in series.** If the 800-gal reactors are arranged in series, the conversion in the first reactor is

$$X_1 = \frac{\tau_1 k}{1 + \tau_1 k} \quad (\text{E4-2.6})$$

where

$$\tau = \frac{V_1}{v_{01}} = \left(800 \text{ gal} \times \frac{1 \text{ ft}^3}{7.48 \text{ gal}} \right) \times \frac{1}{15.34 \text{ ft}^3/\text{min}} = 6.97 \text{ min}$$

The **Damköhler number** is

$$\text{Da}_1 = \tau_1 k = 6.97 \text{ min} \times \frac{0.311}{\text{min}} = 2.167$$

$$X_1 = \frac{2.167}{1 + 2.167} = 0.684$$

To calculate the conversion exiting the second reactor, we recall that $V_1 = V_2 = V$ and $v_{01} = v_{02} = v_0$; then

$$\tau_1 = \tau_2 = \tau$$

Combining the mole balance on the second reactor with the rate law, we obtain

$$V = \frac{F_{A0}(X_2 - X_1)}{-r_{A2}} = \frac{C_{A0}v_0(X_2 - X_1)}{kC_{A0}(1 - X_2)} = \frac{v_0}{k} \left(\frac{X_2 - X_1}{1 - X_2} \right) \quad (\text{E4-2.7})$$

Solving for the conversion exiting the second reactor yields

$$X_2 = \frac{X_1 + \tau k}{1 + \tau k} = \frac{0.684 + 2.167}{1 + 2.167} = 0.90$$

The same result could have been obtained from Equation (4-11):

$$X = 1 - \frac{1}{(1 + \tau k)^n} = 1 - \frac{1}{(1 + 2.167)^2} = 0.90$$

Two million pounds of ethylene glycol per year can be produced using two 800-gal (3.0-m³) reactors in series.

Conversion in the series arrangement is greater than in parallel for CSTRs.

From our discussion of reactor staging in Chapter 2, we could have predicted that the series arrangement would have given the higher conversion.

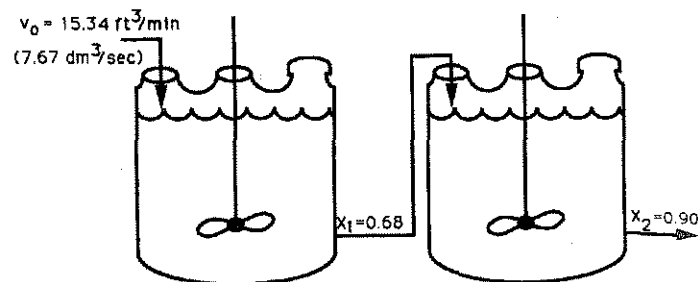


Figure E4-2.3 CSTRs in series.

Two equal-sized CSTRs in series will give a higher conversion than two CSTRs in parallel of the same size when the reaction order is greater than zero.

We can find information about the safety of ethylene glycol and other chemicals from the World Wide Web (WWW) (Table 4-4). One source is the Vermont Safety information on the Internet (Vermont SIRI). For example, we can learn from the *Control Measures* that we should use neoprene gloves when handling the material, and that we should avoid breathing the vapors. If we

TABLE 4-4. ACCESSING SAFETY INFORMATION

Safety Information
MSDS

1. Type in
<http://www.siri.org/>
2. When the first screen appears, click on "Material Safety Data Sheets." ("MSDS")
3. When the next page appears, type in the chemical you want to find.
Example: Find ethylene glycol
Then click on Enter.
4. The next page will show a list of a number of companies that provide the data on ethylene glycol.
EXCITON CHEMICAL
KALAMA INTERNATIONAL
DOW CHEMICAL USA
etc.
Let's click on "EXCITON." The materials safety data sheet provided by EXCITON will appear.
5. Scroll "ethylene glycol" for information you desire.
General Information
Ingredients Information
Physical/Chemical Characteristics
Fire and Explosion Hazard Data
Reactivity Data
Health Hazard Data
Control Measures
Transportation Data
Disposal Data
Label Data

click on "Dow Chemical USA" and scroll the *Reactivity Data*, we would find that ethylene glycol will ignite in air at 413°C.

4.3 Tubular Reactors

Gas-phase reactions are carried out primarily in tubular reactors where the flow is generally turbulent. By assuming that there is no dispersion and there are no radial gradients in either temperature, velocity, or concentration, we can model the flow in the reactor as plug-flow. Laminar reactors are discussed in Chapter 13 and dispersion effects in Chapter 14. The differential form of the design equation

PFR mole
balance

$$F_{A0} \frac{dX}{dV} = -r_A$$

must be used when there is a pressure drop in the reactor or heat exchange between the PFR and the surroundings. In the absence of pressure drop or heat exchange the integral form of the *plug flow design* equation is used,

PFR design
equation

$$V = F_{A0} \int_0^X \frac{dX}{-r_A}$$

Substituting the rate law for the special case of a second-order reaction gives us

Rate law

$$V = F_{A0} \int_0^X \frac{dX}{kC_A^2}$$

For constant-temperature and constant-pressure gas-phase reactions, the concentration is expressed as a function of conversion:

Stoichiometry
(gas-phase)

$$C_A = \frac{F_A}{v} = \frac{F_{A0}(1-X)}{v_0(1+\epsilon X)} = C_{A0} \frac{(1-X)}{(1+\epsilon X)}$$

and then substituted into the design equation:

Combine

$$V = F_{A0} \int_0^X \frac{(1+\epsilon X)^2}{kC_{A0}^2(1-X)^2} dX$$

The entering concentration C_{A0} can be taken outside the integral sign since it is not a function of conversion. Since the reaction is carried out isothermally, the specific reaction rate constant, k , can also be taken outside the integral sign.

For an isothermal
reaction, k is
constant

$$V = \frac{F_{A0}}{kC_{A0}^2} \int_0^X \frac{(1+\epsilon X)^2}{(1-X)^2} dX$$

From the integral equations in Appendix A.1, we find that

Reactor volume
for a second-order
gas-phase reaction

$$V = \frac{v_0}{kC_{A0}} \left[2\varepsilon(1+\varepsilon) \ln(1-X) + \varepsilon^2 X + \frac{(1+\varepsilon)^2 X}{1-X} \right] \quad (4-17)$$

If we divide both sides of Equation (4-17) by the cross-sectional area of the reactor, A_c , we obtain the following equation relating reactor length to conversion:

$$L = \frac{v_0}{kC_{A0}A_c} \left[2\varepsilon(1+\varepsilon) \ln(1-X) + \varepsilon^2 X + \frac{(1+\varepsilon)^2 X}{1-X} \right]$$

A plot of conversion along the length of the reactor is shown for four different reactions and values of ε in Figure 4-7 to illustrate the effects of volume

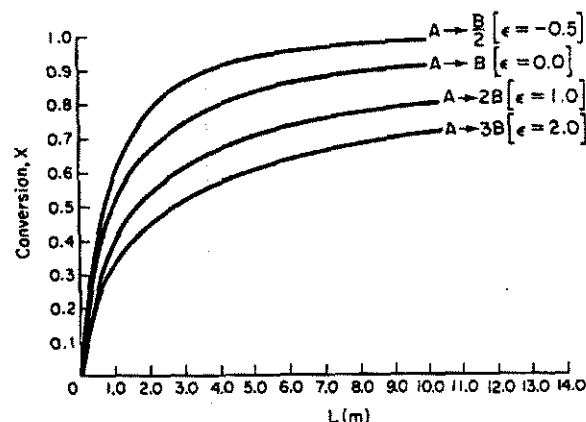


Figure 4-7 Conversion as a function of distance down the reactor.

change on reaction parameters. The following typical parameter values were chosen to arrive at these curves:

$$\begin{aligned} k &= 5.0 \text{ dm}^3/\text{mol} \cdot \text{s} & A_c &= 1.0 \text{ dm}^2 \\ C_{A0} &= 0.2 \text{ mol/dm}^3 & v_0 &= 1 \text{ dm}^3/\text{s} \end{aligned}$$

$$L = 1.0 \left[2\varepsilon(1+\varepsilon) \ln(1-X) + \varepsilon^2 X + \frac{(1+\varepsilon)^2 X}{1-X} \right] \text{ meters}$$

We observe from this figure that for **identical rate-law parameters**, the reaction that has a decrease in the total number of moles (i.e., $\varepsilon = -0.5$) will have the highest conversion for a fixed reactor length. This relationship should be expected for fixed temperature and pressure because the volumetric flow rate,

$$v = (1 - 0.5X)v_0$$

decreases with increasing conversion, and the reactant spends more time in the reactor than reactants that produce no net change in the total number of moles (e.g., $A \rightarrow B$ and $\varepsilon = 0$). Similarly, reactants that produce an increase in the total number of moles upon reaction (e.g., $\varepsilon = 2$) will spend less time in the reactor than reactants of reactions for which ε is zero or negative.

Example 4-3 Neglecting Volume Change with Reaction

The gas-phase cracking reaction



is to be carried out in a tubular reactor. The reaction is second-order and the parameter values are the same as those used to construct Figure 4-7. If 60% conversion is desired, what error will result if volume change is neglected ($\varepsilon = 0$) in sizing the reactor?

Solution

In Figure E4-3.1 (taken from Figure 4-7), we see that a reactor length of 1.5 m is required to achieve 60% conversion for $\varepsilon = 0$. However, by correctly accounting for volume change [$\varepsilon = (1)(2 + 1 - 1) = 2$], we see that a reactor length of 5.0 m would be required. If we had used the 1.5-m-long reactor, we would have achieved only 40% conversion.

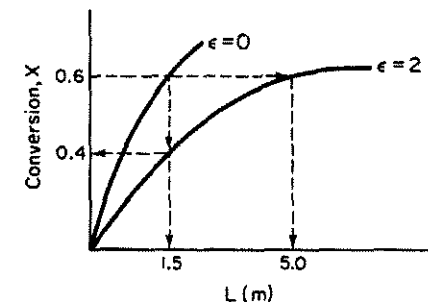


Figure E4-3.1

Example 4-4 Producing 300 Million Pounds per Year of Ethylene in a Plug-Flow Reactor: Design of a Full-Scale Tubular Reactor

Ethylene ranks fourth in the United States in total pounds of chemicals produced each year and it is the number one organic chemical produced each year. Over 35 billion pounds were produced in 1997 and sold for \$0.25 per pound. Sixty-five percent of the ethylene produced is used in the manufacture of fabricated plastics, 20% for ethylene oxide and ethylene glycol, 5% for fibers, and 5% for solvents.

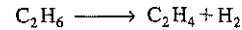
Look at
the poor
design that
could result

The economics

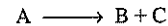
The uses

Determine the plug-flow reactor volume necessary to produce 300 million pounds of ethylene a year from cracking a feed stream of pure ethane. The reaction is irreversible and follows an elementary rate law. We want to achieve 80% conversion of ethane, operating the reactor isothermally at 1100 K at a pressure of 6 atm.

Solution



Let $A = \text{C}_2\text{H}_6$, $B = \text{C}_2\text{H}_4$, and $C = \text{H}_2$. In symbols,



The molar flow rate of ethylene exiting the reactor is

$$\begin{aligned} F_B &= 300 \times 10^6 \frac{\text{lb}}{\text{year}} \times \frac{1 \text{ year}}{365 \text{ days}} \times \frac{1 \text{ day}}{24 \text{ h}} \times \frac{1 \text{ h}}{3600 \text{ s}} \times \frac{\text{lb mol}}{28 \text{ lb}} \\ &= 0.340 \frac{\text{lb mol}}{\text{s}} \end{aligned}$$

Next calculate the molar feed rate of ethane. To produce 0.34 lb mol/s of ethylene when 80% conversion is achieved,

$$\begin{aligned} F_B &= F_{A0} X \\ F_{A0} &= \frac{0.34}{0.8} = 0.425 \frac{\text{lb mol}}{\text{s}} \end{aligned}$$

1. Plug-flow design equation:

$$F_{A0} \frac{dX}{dV} = -r_A$$

Rearranging and integrating for the case of no pressure drop and isothermal operation yields

$$V = F_{A0} \int_0^X \frac{dX}{-r_A} \quad (\text{E4-4.1})$$

2. Rate law:¹

$$-r_A = kC_A \quad \text{with} \quad k = 0.072 \text{ s}^{-1} \text{ at } 1000 \text{ K} \quad (\text{E4-4.2})$$

The activation energy is 82 kcal/g mol.

3. Stoichiometry.

For isothermal operation and negligible pressure drop, the concentration of ethane is calculated as follows:

Combining the design equation, rate law, and stoichiometry

Analytical solution

¹ Ind. Eng. Chem. Process Des. Dev., 14, 218 (1975); Ind. Eng. Chem., 59(5), 70 (1967).

Gas phase, constant T and P :

$$v = v_0 \frac{F_T}{F_{T0}} = v_0(1 + \varepsilon X)$$

$$C_A = \frac{F_A}{v} = \frac{F_{A0}(1-X)}{v_0(1+\varepsilon X)} = C_{A0} \left(\frac{1-X}{1+\varepsilon X} \right) \quad (\text{E4-4.3})$$

$$C_C = \frac{C_{A0}X}{(1+\varepsilon X)} \quad (\text{E4-4.4})$$

4. We now combine Equations (E4-4.1) through (E4-4.3) to obtain

$$\begin{aligned} V &= F_{A0} \int_0^X \frac{dX}{kC_{A0}(1-X)/(1+\varepsilon X)} = F_{A0} \int_0^X \frac{(1+\varepsilon X)dX}{kC_{A0}(1-X)} \\ &= \frac{F_{A0}}{C_{A0}} \int_0^X \frac{(1+\varepsilon X)dX}{k(1-X)} \end{aligned} \quad (\text{E4-4.5})$$

Since the reaction is carried out isothermally, we can take k outside the integral sign and use Appendix A.1 to carry out our integration.

$$V = \frac{F_{A0}}{kC_{A0}} \int_0^X \frac{(1+\varepsilon X)dX}{1-X} = \frac{F_{A0}}{kC_{A0}} \left[(1+\varepsilon) \ln \frac{1}{1-X} - \varepsilon X \right] \quad (\text{E4-4.6})$$

5. Parameter evaluation:

$$\begin{aligned} C_{A0} &= y_{A0} C_{T0} = \frac{y_{A0} P_0}{RT_0} = (1) \left(\frac{6 \text{ atm}}{0.73 \text{ ft}^3 \cdot \text{atm} / \text{lb mol} \cdot ^\circ\text{R} \times 1980^\circ\text{R}} \right) \\ &= 0.00415 \frac{\text{lb mol}}{\text{ft}^3} \end{aligned}$$

$$\varepsilon = y_{A0} \delta = (1)(1+1-1) = 1$$

We need to calculate k at 1100 K.

$$\begin{aligned} k(T_2) &= k(T_1) \exp \left[\frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \right] \\ &= k(T_1) \exp \left[\frac{E}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right) \right] \\ &= \frac{0.072}{\text{s}} \exp \left[\frac{82,000 \text{ cal/g mol} (1100 - 1000) \text{ K}}{1.987 \text{ cal/(g mol} \cdot \text{K)} (1000 \text{ K)} (1100 \text{ K)}} \right] \\ &= 3.07 \text{ s}^{-1} \end{aligned} \quad (\text{E4-4.7})$$

Substituting into Equation (E4-4.6) yields

$$V = \frac{0.425 \text{ lb mol/s}}{(3.07/\text{s})(0.00415 \text{ lb mol/ft}^3)} \left[(1+1) \ln \frac{1}{1-X} - (1)X \right] \quad (\text{E4-4.8})$$

$$= 33.36 \text{ ft}^3 \left[2 \ln \left(\frac{1}{1-X} \right) - X \right]$$

For $X = 0.8$,

$$V = 33.36 \text{ ft}^3 \left[2 \ln \left(\frac{1}{1-0.8} \right) - 0.8 \right]$$

$$= 80.7 \text{ ft}^3 = (2280 \text{ dm}^3 = 2.28 \text{ m}^3)$$

It was decided to use a bank of 2-in. schedule 80 pipes in parallel that are 40 ft in length. For pipe schedule 80, the cross-sectional area is 0.0205 ft^2 . The number of pipes necessary is

$$n = \frac{80.7 \text{ ft}^3}{(0.0205 \text{ ft}^2)(40 \text{ ft})} = 98.4$$

Equation (E4-4.7) was used along with $A_c = 0.0205 \text{ ft}^2$ and Equations (E4-4.3) and (E4-4.4) to obtain Figure E4-4.1. Using a bank of 100 pipes will give us the reactor

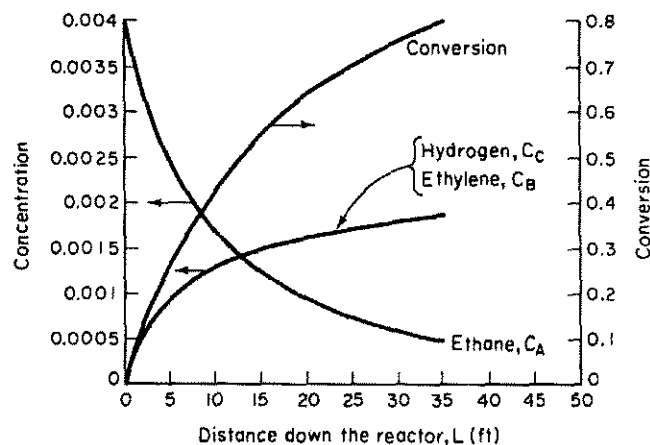
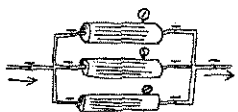


Figure E4-4.1 Conversion and concentration profiles.

volume necessary to make 300 million pounds per year of ethylene from ethane. The concentration and conversion profiles down any one of the pipes are shown in Figure E4-4.1.

The number of PFRs in parallel



Pressure drop is ignored for liquid-phase kinetics calculations

For gas-phase reactions pressure drop may be very important

4.4 Pressure Drop in Reactors

In liquid-phase reactions, the concentration of reactants is insignificantly affected by even relatively large changes in the total pressure. Consequently, we can totally ignore the effect of pressure drop on the rate of reaction when sizing liquid-phase chemical reactors. However, in gas-phase reactions, the concentration of the reacting species is proportional to the total pressure and consequently, proper accounting for the effects of pressure drop on the reaction system can, in many instances, be a key factor in the success or failure of the reactor operation.

4.4.1 Pressure Drop and the Rate Law

We now focus our attention on accounting for the pressure drop in the rate law. For an ideal gas, the concentration of reacting species i is

$$C_i = \frac{F_i}{v} = \frac{F_{A0}(\Theta_i + v_i X)}{v_0(1 + \epsilon X)(P_0/P)(T/T_0)} \quad (3-46)$$

For isothermal operation

$$C_i = C_{A0} \left(\frac{\Theta_i + v_i X}{1 + \epsilon X} \right) \frac{P}{P_0} \quad (4-18)$$

We now must determine the ratio P/P_0 as a function of volume V or the catalyst weight, W , to account for pressure drop. We then can combine the concentration, rate law, and design equation. However, whenever accounting for the effects of pressure drop, the differential form of the mole balance (design equation) must be used.

If, for example, the second-order isomerization reaction



When $P \neq P_0$ one must use the differential forms of the PFR/PBR design equations

is being carried out in a packed-bed reactor, the differential form of the mole balance equation in terms of catalyst weight is

$$F_{A0} \frac{dX}{dW} = -r'_A \left(\frac{\text{gram moles}}{\text{gram catalyst} \cdot \text{min}} \right) \quad (2-17)$$

The rate law is

$$-r'_A = kC_A^2 \quad (4-19)$$

From stoichiometry for gas-phase reactions,

$$C_A = \frac{C_{A0}(1-X)}{1 + \epsilon X} \frac{P}{P_0} \frac{T_0}{T}$$

and the rate law can be written as

$$-r'_A = k \left[\frac{C_{A0}(1-X)}{1+\varepsilon X} \frac{P}{P_0} \frac{T_0}{T} \right]^2 \quad (4-20)$$

Note from Equation (4-20) that the larger the pressure drop (i.e., the smaller P) from frictional losses, the smaller the reaction rate!

Combining Equation (4-20) with the mole balance (2-17) and assuming isothermal operation ($T = T_0$) gives

$$F_{A0} \frac{dX}{dW} = k \left[\frac{C_{A0}(1-X)}{1+\varepsilon X} \right]^2 \left(\frac{P}{P_0} \right)^2$$

Dividing by F_{A0} (i.e., $v_0 C_{A0}$) yields

$$\frac{dX}{dW} = \frac{k C_{A0}}{v_0} \left(\frac{1-X}{1+\varepsilon X} \right)^2 \left(\frac{P}{P_0} \right)^2$$

For isothermal operation ($T = T_0$) the right-hand side is a function of only conversion and pressure:

Another Equation
is needed.
(e.g., $P = f(W)$)

$$\frac{dX}{dW} = F_1(X, P) \quad (4-21)$$

We now need to relate the pressure drop to the catalyst weight in order to determine the conversion as a function of catalyst weight.

4.4.2 Flow Through a Packed Bed

The majority of gas-phase reactions are catalyzed by passing the reactant through a packed bed of catalyst particles. The equation used most to calculate pressure drop in a packed porous bed is the **Ergun equation**:²

Ergun equation
$$\frac{dP}{dz} = - \frac{G}{\rho g_c D_p} \left(\frac{1-\phi}{\phi^3} \right) \left[\frac{150(1-\phi)\mu}{D_p} + 1.75G \right] \quad (4-22)$$

² R. B. Bird, W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena* (New York: Wiley, 1960), p. 200.

where P = pressure, lb/ft²

ϕ = porosity = $\frac{\text{volume of void}}{\text{total bed volume}}$

$1 - \phi$ = $\frac{\text{volume of solid}}{\text{total bed volume}}$

$g_c = 32.174 \text{ lb}_m \cdot \text{ft/s}^2 \cdot \text{lb}_f (\text{conversion factor})$

$= 4.17 \times 10^8 \text{ lb}_m \cdot \text{ft/h}^2 \cdot \text{lb}_f$

(recall that for the metric system $g_c = 1.0$)

D_p = diameter of particle in the bed, ft

μ = viscosity of gas passing through the bed, lb_m/ft · h

z = length down the packed bed of pipe, ft

u = superficial velocity = volumetric flow ÷ cross-sectional area of pipe, ft/h

ρ = gas density, lb/ft³

$G = \rho u$ = superficial mass velocity, (g/cm² · s) or (lb_m/ft² · h)



In calculating the pressure drop using the Ergun equation, the only parameter that varies with pressure on the right-hand side of Equation (4-22) is the gas density, ρ . We are now going to calculate the pressure drop through the bed.

Because the reactor is operated at steady state, the mass flow rate at any point down the reactor, \dot{m} (kg/s), is equal to the entering mass flow rate, \dot{m}_0 (i.e., equation of continuity),

$$\dot{m}_0 = \dot{m}$$

$$\rho_0 v_0 = \rho v$$

Recalling Equation (3-41), we have

$$v = v_0 \frac{P_0}{P} \left(\frac{T}{T_0} \right) \frac{F_T}{F_{T0}} \quad (3-41)$$

$$\rho = \rho_0 \frac{v_0}{v} = \rho_0 \frac{P}{P_0} \left(\frac{T_0}{T} \right) \frac{F_{T0}}{F_T} \quad (4-23)$$

Combining Equations (4-22) and (4-23) gives

$$\frac{dP}{dz} = -\frac{G(1-\phi)}{\rho_0 g_c D_p \phi^3} \left[\frac{150(1-\phi)\mu}{D_p} + 1.752G \right] \frac{P_0}{P} \left(\frac{T}{T_0} \right) \frac{F_T}{F_{T0}}$$

Simplifying yields

$$\frac{dP}{dz} = -\beta_0 \frac{P_0}{P} \left(\frac{T}{T_0} \right) \frac{F_T}{F_{T0}} \quad (4-24)$$

where

$$\beta_0 = \frac{G(1-\phi)}{\rho_0 g_c D_p \phi^3} \left[\frac{150(1-\phi)\mu}{D_p} + 1.752G \right] \quad (4-25)$$

For tubular packed-bed reactors we are more interested in catalyst weight rather than the distance z down the reactor. The catalyst weight up to a distance of z down the reactor is

Use this form for multiple reactions and membrane reactors

$$\begin{aligned} W &= (1-\phi)A_c z \times \rho_c \\ \left[\begin{array}{c} \text{weight of} \\ \text{catalyst} \end{array} \right] &= \left[\begin{array}{c} \text{volume of} \\ \text{solids} \end{array} \right] \times \left[\begin{array}{c} \text{density of} \\ \text{solid catalyst} \end{array} \right] \end{aligned} \quad (4-26)$$

where A_c is the cross-sectional area. The bulk density of the catalyst, ρ_b (mass of catalyst per volume of reactor bed), is just the product of the solid density, ρ_c , the fraction of solids, $(1-\phi)$:

$$\rho_b = \rho_c (1-\phi)$$

Using the relationship between z and W [Equation (4-26)] we can change our variables to express the Ergun equation in terms of catalyst weight:

$$\frac{dP}{dW} = -\frac{\beta_0}{A_c(1-\phi)\rho_c} \frac{P_0}{P} \left(\frac{T}{T_0} \right) \frac{F_T}{F_{T0}} \quad (4-27)$$

Further simplification yields

$$\frac{dP}{dW} = -\frac{\alpha}{2} \frac{T}{T_0} \frac{P_0}{P/P_0} \left(\frac{F_T}{F_{T0}} \right) \quad (4-28)$$

where

$$\alpha = \frac{2\beta_0}{A_c \rho_c (1-\phi) P_0} \quad (4-29)$$

Equation (4-28) will be the one we use when multiple reactions are occurring or when there is pressure drop in a membrane reactor. However, for single reactions in packed-bed reactors it is more convenient to express the Ergun equation in terms of the conversion X . Recalling Equation (3-42) for F_T ,

$$F_T = F_{T0} + F_{A0}\delta X = F_{T0} \left(1 + \frac{F_{A0}}{F_{T0}} \delta X \right) \quad (3-42)$$

and the development leading to Equation (3-43),

$$\frac{F_T}{F_{T0}} = 1 + \varepsilon X$$

where, as before,

$$\varepsilon = y_{A0}\delta = \frac{F_{A0}}{F_{T0}}\delta$$

Equation (4-28) can now be written as

Differential form of Ergun equation for the pressure drop in packed beds

$$\frac{dP}{dW} = -\frac{\alpha}{2} \frac{T}{T_0} \frac{P_0}{P/P_0} (1 + \varepsilon X) \quad (4-30)$$

We note that when ε is negative the pressure drop ΔP will be less (i.e., higher pressure) than that for $\varepsilon = 0$. When ε is positive, the pressure drop ΔP will be greater than when $\varepsilon = 0$.

For isothermal operation, Equation (4-30) is only a function of conversion and pressure:

$$\frac{dP}{dW} = F_2(X, P) \quad (4-31)$$

Recalling Equation (4-21),

Two coupled equations to be solved numerically

$$\frac{dX}{dW} = F_1(X, P) \quad (4-21)$$

we see that we have two coupled first-order differential equations, (4-31) and (4-21), that must be solved simultaneously. A variety of software packages and numerical integration schemes are available for this purpose.

Analytical Solution. If $\varepsilon = 0$, or if we can neglect (εX) with respect to 1.0 (i.e., $1 \gg \varepsilon X$), we can obtain an analytical solution to Equation (4-30) for isothermal operation (i.e., $T = T_0$). For isothermal operation with $\varepsilon = 0$, Equation (4-30) becomes

Isothermal with
 $\varepsilon = 0$

$$\frac{dP}{dW} = -\frac{\alpha P_0}{2(P/P_0)} \quad (4-32)$$

Rearranging gives us

$$\frac{2P}{P_0} \frac{d(P/P_0)}{dW} = -\alpha$$

Taking P/P_0 inside the derivative, we have

$$\frac{d(P/P_0)^2}{dW} = -\alpha$$

Integrating with $P = P_0$ at $W = 0$ yields

$$\left(\frac{P}{P_0}\right)^2 = 1 - \alpha W$$

Taking the square root of both sides gives

$$\frac{P}{P_0} = (1 - \alpha W)^{1/2} \quad (4-33)$$

Pressure ratio
only for $\varepsilon = 0$

where again

$$\alpha = \frac{2\beta_0}{A_c(1-\phi)\rho_c P_0}$$

Equation (4-33) can be used to substitute for the pressure in the rate law, in which case the mole balance can be written solely as a function of conversion and catalyst weight. The resulting equation can readily be solved either analytically or numerically.

If we wish to express the pressure in terms of reactor length z , we can use Equation (4-26) to substitute for W in Equation (4-33). Then

$$\frac{P}{P_0} = \left(1 - \frac{2\beta_0 z}{P_0}\right)^{1/2} \quad (4-34)$$

Example 4-5 Calculating Pressure Drop in a Packed Bed

Calculate the pressure drop in a 60 ft length of 1 1/2-in. schedule 40 pipe packed with catalyst pellets 1/4-in. in diameter when 104.4 lb/h of gas is passing through the bed. The temperature is constant along the length of pipe at 260°C. The void fraction is 45% and the properties of the gas are similar to those of air at this temperature. The entering pressure is 10 atm.

Solution

At the end of the reactor $z = L$ and Equation (4-34) becomes

$$\frac{P}{P_0} = \left(1 - \frac{2\beta_0 L}{P_0}\right)^{1/2} \quad (E4-5.1)$$

$$\beta_0 = \frac{G(1-\phi)}{g_c \rho_0 D_p \phi^3} \left[\frac{150(1-\phi)\mu}{D_p} + 1.75G \right] \quad (4-25)$$

$$G = \frac{\dot{m}}{A_c} \quad (E4-5.2)$$

For 1 1/2-in. schedule 40 pipe, $A_c = 0.01414 \text{ ft}^2$:

$$G = \frac{104.4 \text{ lb}_m/\text{h}}{0.01414 \text{ ft}^2} = 7383.3 \frac{\text{lb}_m}{\text{h} \cdot \text{ft}^2}$$

For air at 260°C and 10 atm,

$$\begin{aligned} \mu &= 0.0673 \text{ lb}_m/\text{ft} \cdot \text{h} \\ \rho_0 &= 0.413 \text{ lb}_m/\text{ft}^3 \end{aligned} \quad (E4-5.3)$$

From the problem statement,

$$\begin{aligned} D_p &\approx \frac{1}{2} \text{ in.} = 0.0208 \text{ ft} \\ g_c &\approx 4.17 \times 10^8 \frac{\text{lb}_m \cdot \text{ft}}{\text{lb}_f \cdot \text{h}^2} \end{aligned}$$

Substituting the values above into Equation (4-25) gives us

$$\begin{aligned} \beta_0 &= \left[\frac{7383.3 \text{ lb}_m/\text{ft}^2 \cdot \text{h} (1 - 0.45)}{(4.17 \times 10^8 \text{ lb}_m \cdot \text{ft}/\text{lb}_f \cdot \text{h}^2)(0.413 \text{ lb}_m/\text{ft}^3)(0.0208 \text{ ft})(0.45)^3} \right] \\ &\times \left[\frac{150(1 - 0.45)(0.0673 \text{ lb}_m/\text{ft} \cdot \text{h})}{0.0208 \text{ ft}} + 1.75(7383.3) \frac{\text{lb}_m}{\text{ft}^2 \cdot \text{h}} \right] \end{aligned} \quad (E4-5.3)$$

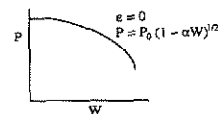
$$\begin{aligned} &= 0.01244 \frac{\text{lb}_f \cdot \text{h}}{\text{ft} \cdot \text{lb}_m} (266.9 + 12,920.8) \frac{\text{lb}_m}{\text{ft}^2 \cdot \text{h}} = 164.1 \frac{\text{lb}_f}{\text{ft}^3} \\ &= 164.1 \frac{\text{lb}_f}{\text{ft}^3} \times \frac{1 \text{ ft}^2}{144 \text{ in.}^2} \times \frac{1 \text{ atm}}{14.7 \text{ lb}_f/\text{in.}^2} \\ &= 0.0775 \frac{\text{atm}}{\text{ft}} = 25.8 \frac{\text{kPa}}{\text{m}} \end{aligned} \quad (E4-5.4)$$

Evaluating
the pressure drop
parameters

$$\frac{P}{P_0} = \left(1 - \frac{2\beta_0 L}{P_0}\right)^{1/2} = \left(1 - \frac{2 \times 0.0775 \text{ atm/ft} \times 60 \text{ ft}}{10 \text{ atm}}\right)^{1/2} \quad (\text{E4-5.5})$$

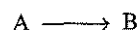
$$P = 0.265 P_0 = 2.65 \text{ atm} \quad (\text{E4-5.6})$$

$$\Delta P = P_0 - P = 10 - 2.65 = 7.35 \text{ atm}$$

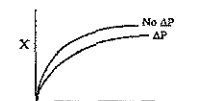
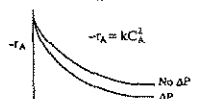
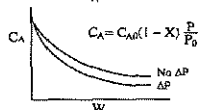


Reaction with Pressure Drop

Analytical solution: Now that we have expressed pressure as a function of catalyst weight [Equation (4-33)] we can return to the second-order isothermal reaction,



to relate conversion and catalyst weight. Recall our mole balance, rate law, and stoichiometry.



Mole balance: $F_{A0} \frac{dX}{dW} = -r'_A \quad (2-17)$

Rate law: $-r'_A = kC_A^2 \quad (4-19)$

Stoichiometry. Gas-phase isothermal reaction with $\varepsilon = 0$:

$$C_A = C_{A0}(1 - X) \frac{P}{P_0} \quad (4-35)$$

Using Equation (4-33) to substitute for P/P_0 in terms of the catalyst weight, we obtain

$$C_A = C_{A0}(1 - X)(1 - \alpha W)^{1/2}$$

Only
for
 $\varepsilon = 0$

Combining: $\frac{dX}{dW} = \frac{kC_{A0}^2}{F_{A0}} (1 - X)^2 [(1 - \alpha W)^{1/2}]^2$

Separating variables: $\frac{F_{A0}}{kC_{A0}^2} \frac{dX}{(1 - X)^2} = (1 - \alpha W) dW$

Integrating with limits $X = 0$ when $W = 0$ and substituting for $F_{A0} = C_{A0}v_0$ yields

$$\frac{v_0}{kC_{A0}} \left(\frac{X}{1 - X} \right) = W \left(1 - \frac{\alpha W}{2} \right)$$

Solving for conversion gives

$$X = \frac{\frac{kC_{A0}W}{v_0} \left(1 - \frac{\alpha W}{2} \right)}{1 + \frac{kC_{A0}W}{v_0} \left(1 - \frac{\alpha W}{2} \right)} \quad (4-36)$$

Solving for the catalyst weight, we have

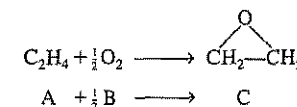
$$W = \frac{1 - \{1 - [(2v_0\alpha)/kC_{A0}][X/(1 - X)]\}^{1/2}}{\alpha} \quad (4-37)$$

Catalyst weight for
second-order
reaction in PFR
with ΔP

We now proceed (Example 4-6) to combine pressure drop with reaction in a packed bed for the case where we will assume that $\varepsilon X \ll 1$ in the Ergun equation but not in the rate law in order to obtain an analytical solution. Example 4-7 removes this assumption and solves Equations (4-21) and (4-31) numerically.

Example 4-6 Calculating X in a Reactor with Pressure Drop

Approximately 7 billion pounds of ethylene oxide were produced in the United States in 1997. The 1997 selling price was \$0.58 a pound, amounting to a commercial value of \$4.0 billion. Over 60% of the ethylene oxide produced is used to make ethylene glycol. The major end uses of ethylene oxide are antifreeze (30%), polyester (30%), surfactants (10%), and solvents (5%). We want to calculate the catalyst weight necessary to achieve 60% conversion when ethylene oxide is to be made by the vapor-phase catalytic oxidation of ethylene with air.



Ethylene and oxygen are fed in stoichiometric proportions to a packed-bed reactor operated isothermally at 260°C. Ethylene is fed at a rate of 0.30 lb mol/s at a pressure of 10 atm. It is proposed to use 10 banks of 1½-in.-diameter schedule 40 tubes packed with catalyst with 100 tubes per bank. Consequently, the molar flow rate to each tube is to be 3×10^{-4} lb mol/s. The properties of the reacting fluid are to be considered identical to those of air at this temperature and pressure. The density of the ½-in.-catalyst particles is 120 lb/ft³ and the bed void fraction is 0.45. The rate law is

$$-r'_A = kP_A^{1/3}P_B^{2/3} \quad \text{lb mol/lb cat} \cdot \text{h}$$

with³

$$k = 0.0141 \frac{\text{lb mol}}{\text{atm} \cdot \text{lb cat} \cdot \text{h}} \text{ at } 260^\circ\text{C}$$

³ Ind. Eng. Chem., 45, 234 (1953).

Solution

1. Differential mole balance:

$$F_{A0} \frac{dX}{dW} = -r'_A \quad (\text{E4-6.1})$$

2. Rate law:

$$-r'_A = k P_A^{1/3} P_B^{2/3} = k (C_A RT)^{1/3} (C_B RT)^{2/3} \quad (\text{E4-6.2})$$

$$= k RT C_A^{1/3} C_B^{2/3} \quad (\text{E4-6.3})$$

3. Stoichiometry. Gas-phase, isothermal $v = v_0(1 + \varepsilon X)(P_0/P)$:

$$C_A = \frac{F_A}{v} = \frac{C_{A0}(1-X)}{1 + \varepsilon X} \left(\frac{P}{P_0} \right) \quad (\text{E4-6.4})$$

$$C_B = \frac{F_B}{v} = \frac{C_{A0}(\Theta_B - X/2)}{1 + \varepsilon X} \left(\frac{P}{P_0} \right) \quad (\text{E4-6.5})$$

4. Combining the rate law and concentrations:

$$-r'_A = k RT_0 \left[\frac{C_{A0}(1-X)}{1 + \varepsilon X} \left(\frac{P}{P_0} \right) \right]^{1/3} \cdot \left[\frac{C_{A0}(\Theta_B - X/2)}{1 + \varepsilon X} \left(\frac{P}{P_0} \right) \right]^{2/3} \quad (\text{E4-6.6})$$

$$= \frac{k C_{A0} RT_0}{1 + \varepsilon X} \left(\frac{P}{P_0} \right) (1-X)^{1/3} \left(\Theta_B - \frac{X}{2} \right)^{2/3} \quad (\text{E4-6.7})$$

For stoichiometric feed, $\Theta_B = \frac{1}{2}$:

$$-r'_A = k P_{A0} \frac{(1-X)^{1/3} (1/2 - X/2)^{2/3}}{1 + \varepsilon X} \left(\frac{P}{P_0} \right) \quad (\text{E4-6.8})$$

$$= k' \left(\frac{1-X}{1 + \varepsilon X} \right) \frac{P}{P_0}$$

where $k' = k P_{A0} (\frac{1}{2})^{2/3} = 0.63 k P_{A0}$.

5. Developing the design equation. For a packed-bed reactor, the relationship between P and W when $\varepsilon X \ll 1$ is

$$\frac{P}{P_0} = (1 - \alpha W)^{1/2} \quad (\text{4-33})$$

(Note that we will check this assumption in Example 4-7.) Combining Equations (E4-6.8) and (4-33) gives us

$$-r'_A = k' \left(\frac{1-X}{1 + \varepsilon X} \right) (1 - \alpha W)^{1/2} \quad (\text{E4-6.9})$$

Combining Equations (E4-6.9) and (E4-6.1), we have

Eq. (4-33) is valid only if $\varepsilon = 0$ or $\varepsilon X \ll 1$

$$F_{A0} \frac{dX}{dW} = -r'_A = k' \left(\frac{1-X}{1 + \varepsilon X} \right) (1 - \alpha W)^{1/2}$$

Separating variables to form the integrals yields

$$\int_0^X \frac{F_{A0} (1 + \varepsilon X) dX}{k' (1-X)} = \int_0^W (1 - \alpha W)^{1/2} dW$$

Integrating gives us

$$\frac{F_{A0}}{k'} \left[(1 + \varepsilon) \ln \frac{1}{1-X} - \varepsilon X \right] = \frac{2}{3\alpha} [1 - (1 - \alpha W)^{3/2}] \quad (\text{E4-6.10})$$

Solving for W , we obtain

$$W = \frac{1 - [1 - (3\alpha F_{A0}/2k') \{ (1 + \varepsilon) \ln[1/(1-X)] - \varepsilon X \}]^{2/3}}{\alpha} \quad (\text{E4-6.11})$$

6. Parameter evaluation per tube (i.e., divide feed rates by 1000):

Ethylene: $F_{A0} = 3 \times 10^{-4} \text{ lb mol/s} = 1.08 \text{ lb mol/h}$

Oxygen: $F_{B0} = 1.5 \times 10^{-4} \text{ lb mol/s} = 0.54 \text{ lb mol/h}$

I = inerts = N_2 : $F_I = 1.5 \times 10^{-4} \text{ lb mol/s} \times \frac{0.79 \text{ mol } N_2}{0.21 \text{ mol } O_2}$

$$F_I = 5.64 \times 10^{-4} \text{ lb mol/s} = 2.03 \text{ lb mol/h}$$

Summing: $F_{T0} = F_{A0} + F_{B0} + F_I = 3.65 \text{ mol/h}$

$$y_{A0} = \frac{F_{A0}}{F_{T0}} = \frac{1.08}{3.65} = 0.30$$

$$\varepsilon = y_{A0} \delta = (0.3)(1 - \frac{1}{2} - 1) = -0.15$$

$$P_{A0} = y_{A0} P_0 = 3.0 \text{ atm}$$

$$k' = k P_{A0} (\frac{1}{2})^{2/3} = 0.0141 \frac{\text{lb mol}}{\text{atm} \cdot \text{lb cat} \cdot \text{h}} \times 3 \text{ atm} \times 0.63 = 0.0266 \frac{\text{lb mol}}{\text{h} \cdot \text{lb cat}}$$

$$W = \frac{1 - [1 - (3\alpha F_{A0}/2k') \{ (1 - 0.15) \ln[1/(1 - 0.6)] - (-0.15)(0.6) \}]^{2/3}}{\alpha}$$

For 60% conversion, Equation (E4-6.11) becomes

$$W = \frac{1 - (1 - 1.303\alpha F_{A0}/k')^{2/3}}{\alpha} \quad (\text{E4-6.12})$$

In order to calculate α ,

$$\alpha = \frac{2\beta_0}{A_c(1 - \phi)\rho_c P_0}$$

we need the superficial mass velocity, G . The mass flow rates of each entering species are:

Evaluating the pressure drop parameters

$$\dot{m}_{A0} = 1.08 \frac{\text{lb mol}}{\text{h}} \times 28 \frac{\text{lb}}{\text{lb mol}} = 30.24 \text{ lb/h}$$

$$\dot{m}_{B0} = 0.54 \frac{\text{lb mol}}{\text{h}} \times 32 \frac{\text{lb}}{\text{lb mol}} = 17.28 \text{ lb/h}$$

$$\dot{m}_{I0} = 2.03 \frac{\text{lb mol}}{\text{h}} \times 28 \frac{\text{lb}}{\text{lb mol}} = 56.84 \text{ lb/h}$$

The total mass flow rate is

$$\dot{m}_{T0} = 104.4 \frac{\text{lb}}{\text{h}}$$

$$G = \frac{\dot{m}_{T0}}{A_c} = \frac{104.4 \text{ lb/h}}{0.01414 \text{ ft}^2} = 7383.3 \frac{\text{lb}}{\text{h} \cdot \text{ft}^2}$$

This is essentially the same superficial mass velocity, temperature, and pressure as in Example 4-5. Consequently, we can use the value of β_0 calculated in Example 4-5.

$$\beta_0 = 0.0775 \frac{\text{atm}}{\text{ft}}$$

$$\alpha = \frac{2\beta_0}{A_c(1-\phi)\rho_c P_0} = \frac{(2)(0.0775) \text{ atm/ft}}{(0.01414 \text{ ft}^2)(0.55)(120 \text{ lb cat/ft}^3)(10 \text{ atm})} = \frac{0.0166}{\text{lb cat}}$$

Substituting into Equation (E4-6.12) yields

$$W = \frac{1 - \left[1 - \frac{\left(1.303 \frac{0.0166}{\text{lb cat}} \right) \left(1.08 \frac{\text{lb mol}}{\text{h}} \right)}{0.0266 \frac{\text{lb mol}}{\text{lb cat} \cdot \text{h}}} \right]^{2/3}}{0.0166/\text{lb cat}} = 45.4 \text{ lb of catalyst per tube}$$

or 45,400 lb of catalyst total

This catalyst weight corresponds to a pressure drop of approximately 5 atm. If we had neglected pressure drop, the result would have been

$$W = \frac{F_{A0}}{k'} \left[(1+\varepsilon) \ln \frac{1}{1-X} - \varepsilon X \right] = \frac{1.08}{0.0266} \times \left[(1-0.15) \ln \frac{1}{1-0.6} - (-0.15)(0.6) \right] = 35.3 \text{ lb of catalyst per tube (neglecting pressure drop)}$$

and we would have had insufficient catalyst to achieve the desired conversion. Substituting this catalyst weight (i.e., 35,300 lb total) into Equation (E4-6.10) gives a conversion of only 53%.

Neglecting pressure drop results in poor design (here 53% vs. 60% conversion)

Example 4-7 Pressure Drop with Reaction—Numerical Solution

Rework Example 4-6 for the case where volume change is *not* neglected in the Ergun equation and the two coupled differential equations describing the variation of conversion and pressure with catalyst weight are solved numerically.

Solution

Rather than rederive everything starting from the mole balance, rate law, stoichiometry, and pressure drop equations, we will use the equations developed in Example 4-6. Combining Equations (E4-6.1) and (E4-6.8) gives

$$F_{A0} \frac{dX}{dW} = k' \left(\frac{1-X}{1+\varepsilon X} \right) \frac{P}{P_0} \quad (\text{E4-7.1})$$

Recalling Equation (4-30) and assuming isothermal operation gives

$$\frac{dP}{dW} = -\frac{\alpha}{2} \frac{P_0}{(P/P_0)} (1+\varepsilon X) \quad (\text{E4-7.2})$$

Next, we let

$$y = \frac{P}{P_0} \quad \text{and} \quad \alpha = \frac{2\beta_0}{A_c(1-\phi)\rho_c P_0}$$

so that Equations (E4-7.1) and (E4-7.2) can be written as

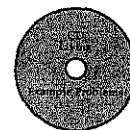
$$\frac{dX}{dW} = \frac{k'}{F_{A0}} \left(\frac{1-X}{1+\varepsilon X} \right) y \quad (\text{E4-7.3})$$

$$\frac{dy}{dW} = -\frac{\alpha(1+\varepsilon X)}{2y} \quad (\text{E4-7.4})$$

For the reaction conditions described in Example 4-6, we have the boundary conditions $W = 0$, $X = 0$, and $y = 1.0$ and the parameter values $\alpha = 0.0166/\text{lb cat}$, $\varepsilon = -0.15$, $k' = 0.0266 \text{ lb mol/h} \cdot \text{lb cat}$, and $F_{A0} = 1.08 \text{ lb mol/h}$.

A large number of ordinary differential equation solver software packages (i.e., ODE solvers) which are extremely user friendly have become available. We shall use POLYMATH⁴ to solve the examples in the printed text. However, the CD-ROM contains an example that uses ASPEN, as well as all the MATLAB and POLYMATH solution programs to the example programs. With POLYMATH one simply enters Equations (E4-7.3) and (E4-7.4) and the corresponding parameter value into the computer (Table E4-7.1) with the initial (rather, boundary) conditions and they are solved and displayed as shown in Figure E4-7.1.

We note that neglecting εX in the Ergun equation in Example 4-6 ($\varepsilon X = -0.09$) to obtain an analytical solution resulted in less than a 10% error.



Program examples POLYMATH, MatLab can be loaded from the CD-ROM (see the Introduction)

⁴ Developed by Professor M. Cutlip of the University of Connecticut, and Professor M. Shacham of Ben Gurion University. Available from the CACHE Corporation, P.O. Box 7939, Austin, TX 78713.

TABLE E4-7.1. POLYMATH SCREEN SHOWING EQUATIONS TYPED IN AND READY TO BE SOLVED.

Equations	Initial Values
$d(y)/d(w) = -\alpha(1+\epsilon x)/2/y$	1
$d(x)/d(w) = \text{rate}/f a_0$	0
$f a_0 = 1.00$	
$\alpha = 0.0166$	
$\epsilon = -0.15$	
$k_{\text{prime}} = 0.0266$	
$f = (1 + \epsilon x)/y$	
$\text{rate} = k_{\text{prime}} * ((1-x)/(1+\epsilon x))^2 * y$	
$w_0 = 0, \quad w_f = 60$	

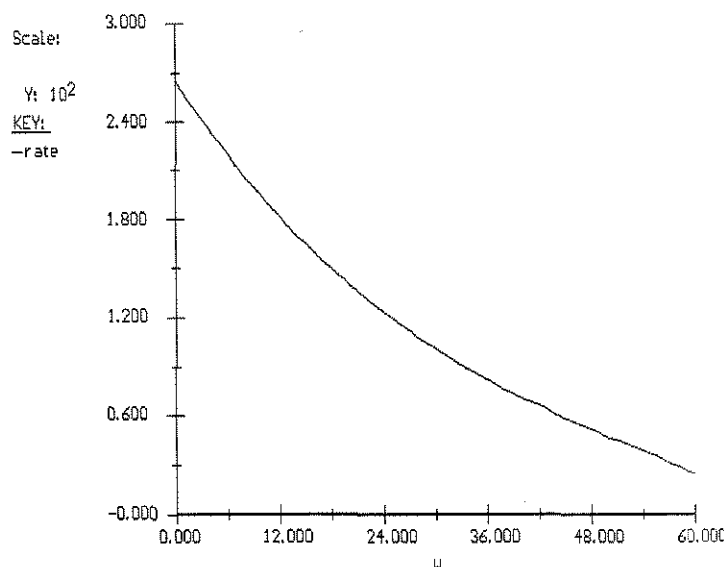


Figure E4-7.1 Reaction rate profile down the PBR.

However, larger errors will result if large values of ϵX are neglected! By taking into account the change in the volumetric flow rate (i.e., $\epsilon = -0.15$) in the pressure drop term, we see that 44.0 lb of catalyst is required per tube as opposed to 45.4 lb when ϵ was neglected in the analytical solution, Equation (E4-7.4). Why was less catalyst required when ϵ was not neglected in Equation (E4-7.4)? The reason is that the numerical solution accounts for the fact that the pressure drop will be less because ϵ is negative.

It is also interesting to learn what happens to the volumetric flow rate along the length of the reactor. Recalling Equation (3-44),

$$v = v_0(1 + \epsilon X) \frac{P_0}{P} \frac{T}{T_0} = \frac{v_0(1 + \epsilon X)(T/T_0)}{P/P_0} \quad (3-44)$$

We let f be the ratio of the volumetric flow rate, v , to the entering volumetric flow rate, v_0 , at any point down the reactor. For isothermal operation Equation (3-44) becomes

$$f = \frac{v}{v_0} = \frac{1 + \epsilon X}{y} \quad (\text{E4-7.5})$$

Figure E4-7.2 shows X , y (i.e., $y = P/P_0$), and f down the length of the reactor. We see that both the conversion and the volumetric flow increase along the length of the reactor while the pressure decreases. For gas-phase reactions with orders greater than zero, this decrease in pressure will cause the reaction rate to be less than in the case of no pressure drop.

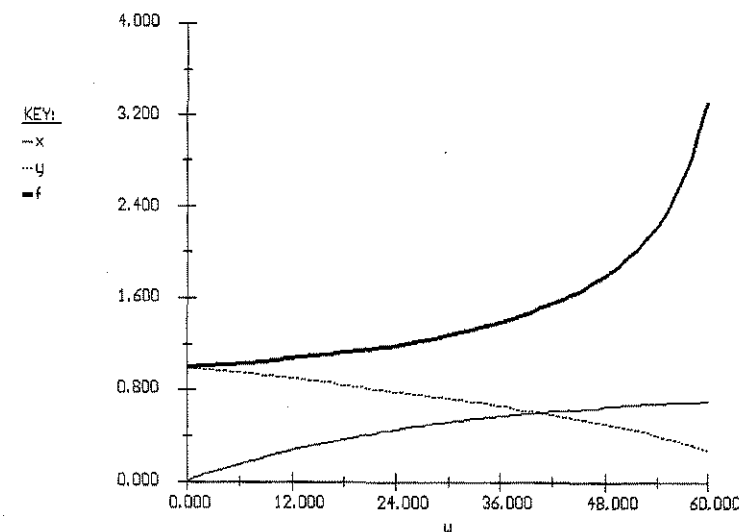


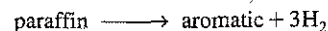
Figure E4-7.2 Output in graphical form from POLYMATH.

Effect of added catalyst on conversion

We note from Figure E4-7.2 that the catalyst weight necessary to raise the conversion the last 1% from 65% to 66% (3.5 lb) is 8.5 times more than that (0.41 lb) required to raise the conversion 1% at the reactor's entrance. Also, during the last 5% increase in conversion, the pressure decreases from 3.8 atm to 2.3 atm.

4.4.3 Spherical Packed-Bed Reactors

When small catalyst pellets are required, the pressure drop can be significant. In Example 4-6 we saw that significant design flaws can result if pressure drop is neglected or if steps are not taken to minimize pressure drop. One type of reactor that minimizes pressure drop and is also inexpensive to build is the spherical reactor, shown in Figure 4-8. In this reactor, called an ultraformer, dehydrogenation reactions such as



are carried out.

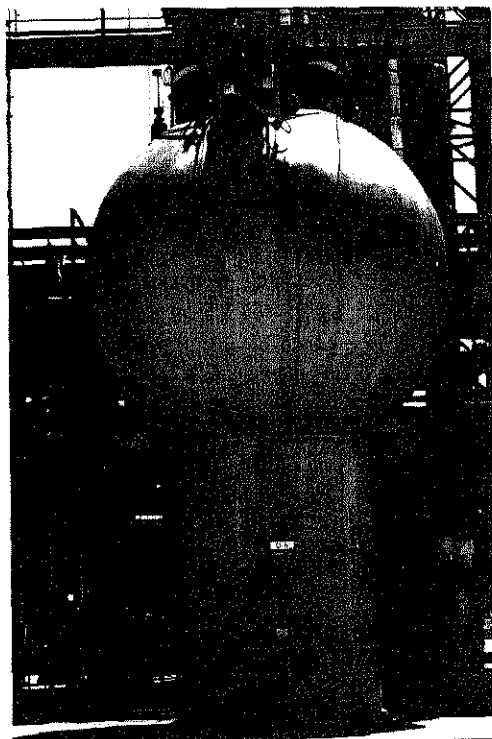


Figure 4-8 Spherical Ultraformer Reactor. (Courtesy of Amoco Petroleum Products.) This reactor is one in a series of six used by Amoco for reforming petroleum naphtha. Photo by K. R. Renicker, Sr.

Another advantage of spherical reactors is that they are the most economical shape for high pressures. As a first approximation we will assume that the fluid moves down through the reactor in plug flow. Consequently, because

of the increase in cross-sectional area, A_c , as the fluid enters the sphere, the superficial velocity, $G = \dot{m}/A_c$, will decrease. From the Ergun equation [Equation (4-22)],

$$\frac{dP}{dz} = -\frac{G(1-\phi)}{\rho g_c D_p \phi^3} \left[\frac{150(1-\phi)\mu}{D_p} + 1.75G \right] \quad (4-22)$$

we know that by decreasing G , the pressure drop will be reduced significantly, resulting in higher conversions.

Because the cross-sectional area of the reactor is small near the inlet and outlet, the presence of catalyst there would cause substantial pressure drop, thereby reducing the efficiency of the spherical reactor. To solve this problem, screens to hold the catalyst are placed near the reactor entrance and exit (Figures 4-9 and 4-10). Here L is the location of the screen from the center of the

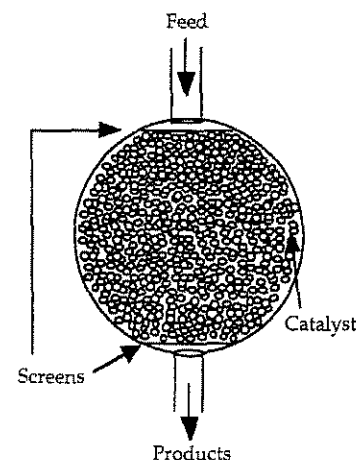


Figure 4-9 Schematic drawing of the inside of a spherical reactor.

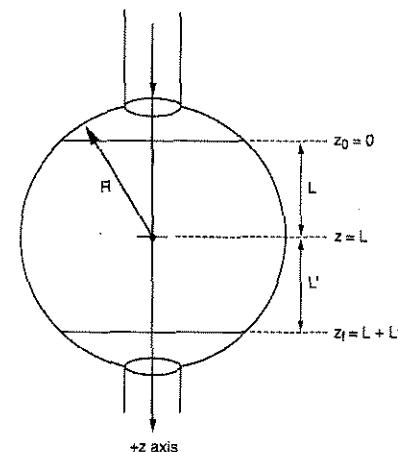


Figure 4-10 Coordinate system and variables used with a spherical reactor. The initial and final integration values are shown as z_0 and z_f .

reactor. We can use elementary geometry and integral calculus to derive the following expressions for cross-sectional area and catalyst weight as a function of the variables defined in Figure 4-10:

$$A_c = \pi[R^2 - (z - L)^2] \quad (4-38)$$

Spherical reactor
catalyst weight

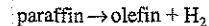
$$W = \rho_c(1-\phi)V = \rho_c(1-\phi)\pi \left[R^2 z - \frac{1}{3}(z-L)^3 - \frac{1}{3}L^3 \right] \quad (4-39)$$

By using these formulas and the standard pressure drop algorithm, one can solve a variety of spherical reactor problems. Note that Equations (4-38) and

(4-39) make use of L and not L' . Thus, one does not need to adjust these formulas to treat spherical reactors that have different amounts of empty space at the entrance and exit (i.e., $L \neq L'$). Only the upper limit of integration needs to be changed, $z_f = L + L'$.

Example 4-8 Dehydrogenation Reactions in a Spherical Reactor

Reforming reactors are used to increase the octane number of petroleum. In a reforming process 20,000 barrels of petroleum are to be processed per day. The corresponding mass and molar feed rates are 44 kg/s and 440 mol/s, respectively. In the reformer, dehydrogenation reactions such as



occur. The reaction is first-order in paraffin. Assume that pure paraffin enters the reactor at a pressure of 2000 kPa and a corresponding concentration of 0.32 mol/dm^3 . Compare the pressure drop and conversion when this reaction is carried out in a tubular packed bed 2.4 m in diameter and 25 m in length with that of a spherical packed bed 6 m in diameter. The catalyst weight is the same in each reactor, 173,870 kg.

$$-r'_A = k' C_A$$

$$-r'_A = \rho_B(-r'_A) = \rho_C(1 - \phi)(-r'_A) = \rho_C(1 - \phi)k' C_A$$

Additional information:

$$\rho_0 = 0.032 \text{ kg/dm}^3$$

$$D_p = 0.02 \text{ dm}$$

$$\phi = 0.4$$

$$k' = 0.02 \text{ dm}^3/\text{kg cat} \cdot \text{s} \quad \mu = 1.5 \times 10^{-6} \text{ kg/dm} \cdot \text{s}$$

$$L = L' = 27 \text{ dm}$$

$$\rho_c = 2.6 \text{ kg/dm}^3$$

Solution

We begin by performing a mole balance over the cylindrical core of thickness Δz shown in Figure E4-8.1.

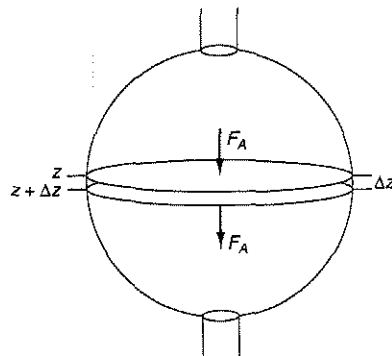


Figure E4-8.1 Spherical reactor.

Following the algorithm

1. Mole balance:

$$\text{In} - \text{out} + \text{generation} = 0$$

$$F_A|_z - F_A|_{z+\Delta z} + r_A A_c \Delta z = 0$$

Dividing by Δz and taking the limit as $\Delta z \rightarrow 0$ yields

$$\frac{dF_A}{dz} = r_A A_c$$

In terms of conversion

$$\frac{dX}{dz} = \frac{-r_A A_c}{F_{A0}} \quad (\text{E4-8.1})$$

2. Rate law:

$$r_A = -k C_A = -k' C_A \rho_c (1 - \phi) \quad (\text{E4-8.2})$$

3. Stoichiometry. Gas, isothermal ($T = T_0$):

$$C_A = C_{A0} \left(\frac{1 - X}{1 + \epsilon X} \right) y \quad (\text{E4-8.3})$$

$$\epsilon = y_{A0} \delta = 1 \times (1 + 1 - 1) = 1 \quad (\text{E4-8.4})$$

where

$$y = \frac{P}{P_0} \quad (\text{E4-8.5})$$

Note that y_{A0} (y with a subscript) represents the mole fraction and y alone represents the pressure ratio, P/P_0 .

The variation in the dimensionless pressure, y , is given by incorporating the variable y in Equation (4-24):

$$\frac{dy}{dz} = -\frac{\beta_0}{P_0 y} (1 + \epsilon X) \quad (\text{E4-8.6})$$

The units of β_0 for this problem are kPa/dm^3 .

$$\beta_0 = \frac{G(1 - \phi)}{\rho_0 g_c D_p \phi^3} \left[\frac{150(1 - \phi)\mu}{D_p} + 1.75 G \right] \quad (\text{E4-8.7})$$

$$G = \frac{\dot{m}}{A_c} \quad (\text{E4-8.8})$$

For a spherical reactor

$$A_c = \pi [R^2 - (z - L)^2] \quad (\text{E4-8.9})$$

$$W = \rho_c(1 - \phi) \pi \left[R^2 z - \frac{1}{3} (z - L)^3 - \frac{1}{3} L^3 \right] \quad (\text{E4-8.10})$$

The equations in boxes are the key equations used in the ODE solver program

Parameter evaluation:

Recall that $g_c = 1$ for metric units.

$$\beta_0 = \left[\frac{G(1-0.4)}{(0.032 \text{ kg/dm}^3)(0.02 \text{ dm})(0.4)^3} \right] \times \left[\frac{150(1-0.4)(1.5 \times 10^{-6} \text{ kg/dm} \cdot \text{s})}{0.02 \text{ dm}} + 1.75G \right] \quad (\text{E4-8.11})$$

$$\beta_0 = [(98.87 \text{ s}^{-1})G + (25,630 \text{ dm}^2/\text{kg})G^2] \times \left(0.01 \frac{\text{kPa/dm}}{\text{kg/dm}^2 \cdot \text{s}^2} \right) \quad (\text{E4-8.12})$$

The last term in brackets converts $(\text{kg/dm}^2 \cdot \text{s})$ to (kPa/dm) . Recalling other parameters, $\dot{m} = 44 \text{ kg/s}$, $L = 27 \text{ dm}$, $R = 30 \text{ dm}$, and $\rho_{\text{cat}} = 2.6 \text{ kg/dm}^3$.

Table E4-8.1 shows the POLYMATH input used to solve the above equations. The MATLAB program is given as a living example problem on the CD-ROM.

TABLE E4-8.1. POLYMATH PROGRAM

Equations	Initial Values
$d(X)/d(z) = -r_A \cdot \text{Ac}/F_{A0}$	0
$d(y)/d(z) = -\beta_0 / (y \cdot (1+K))$	1
$F_{A0} = 440$	
$P_0 = 2000$	
$\text{Ca}0 = 0.32$	
$R = 30$	
$\text{ph}1 = 0.4$	
$\text{kprime} = 0.02$	
$L = 27$	
$\text{rhocat} = 2.6$	
$m = 44$	
$\text{Ca} = \text{Ca}0 \cdot (1-X) \cdot y / (1+K)$	
$\text{Ac} = 3.1416 \cdot (R^2 - (z-L)^2)$	
$V = 3.1416 \cdot (z \cdot R^2 - 1.3 \cdot (z-L)^3 - 1/3 \cdot L^3)$	
$G = m/\text{Ac}$	
$r_A = -\text{kprime} \cdot \text{Ca} \cdot \text{rhocat} \cdot (1-\text{ph}1)$	
$\beta_0 = (98.87 \cdot G + 25630 \cdot G^2) \cdot 0.01$	
$W = \text{rhocat} \cdot (1-\text{ph}1) \cdot V$	
$z_0 = 0, \quad z_f = 54$	

For the spherical reactor, the conversion and the pressure at the exit are

$$X = 0.81 \quad P = 1980 \text{ kPa}$$

If similar calculations are performed for the tubular packed-bed reactor (PBR), one finds that for the same catalyst weight the conversion and pressure at the exit are

$$X = 0.71 \quad P = 308 \text{ kPa}$$

Figure E4-8.2 shows how conversion, X , and dimensionless pressure, y , vary with catalyst weight in each reactor. Here X_1 and y_1 represent the tubular reactor and X_2

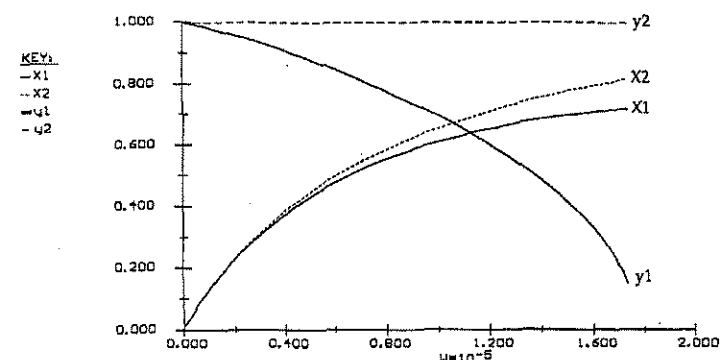


Figure E4-8.2 Pressure and conversion for: 1, tubular PBR; 2, spherical PBR.

and y_2 represent the spherical reactor. In addition to the higher conversion, the spherical reactor has the economic benefit of reducing the pumping and compression cost because of higher pressure at the exit.

Because the pressure drop in the spherical reactor is very small, one could increase the reactant flow rate significantly and still maintain adequate pressure at the exit. In fact, Amoco uses a reactor with similar specifications to process 60,000 barrels of petroleum naphtha per day.

4.4.4 Pressure Drop in Pipes

Normally, the pressure drop for gases flowing through pipes without packing can be neglected. For flow in pipes, the pressure drop along the length of the pipe is given by

$$\frac{dP}{dL} = -G \frac{du}{dL} - \frac{2fG^2}{\rho D} \quad (4-40)$$

where D = pipe diameter, cm

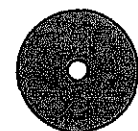
u = average velocity of gas, cm/s

f = Fanning friction factor

$G = \rho u$, $\text{g/cm}^2 \cdot \text{s}$

The friction factor is a function of the Reynolds number and pipe roughness. The mass velocity G is constant along the length of the pipe. Replacing u with G/ρ , and combining with Equation (4-23) for the case of constant T and F_T , Equation (4-40) becomes

$$\rho_0 \frac{dP}{dL} - G^2 \frac{dP}{P dL} + \frac{2fG^2}{D} = 0$$



A comparison between reactors

Integrating with limits $P = P_0$ when $L = 0$, and assuming that f does not vary, we have

$$\frac{P_0^2 - P^2}{2} = G^2 \frac{P_0}{\rho_0} \left(2f \frac{L}{D} + \ln \frac{P_0}{P} \right)$$

Neglecting the second term on the right-hand side gives

$$\frac{P_0^2 - P^2}{2} = 2fG^2 \frac{P_0}{\rho_0} \frac{L}{D}$$

Rearranging, we obtain

$$\frac{P}{P_0} = \left[1 - \frac{4fG^2V}{\rho_0 P_0 A_c D} \right]^{1/2} = (1 - \alpha_p V)^{1/2} \quad (4-41)$$

where

$$\alpha_p = \frac{4fG^2}{A_c \rho_0 P_0 D}$$

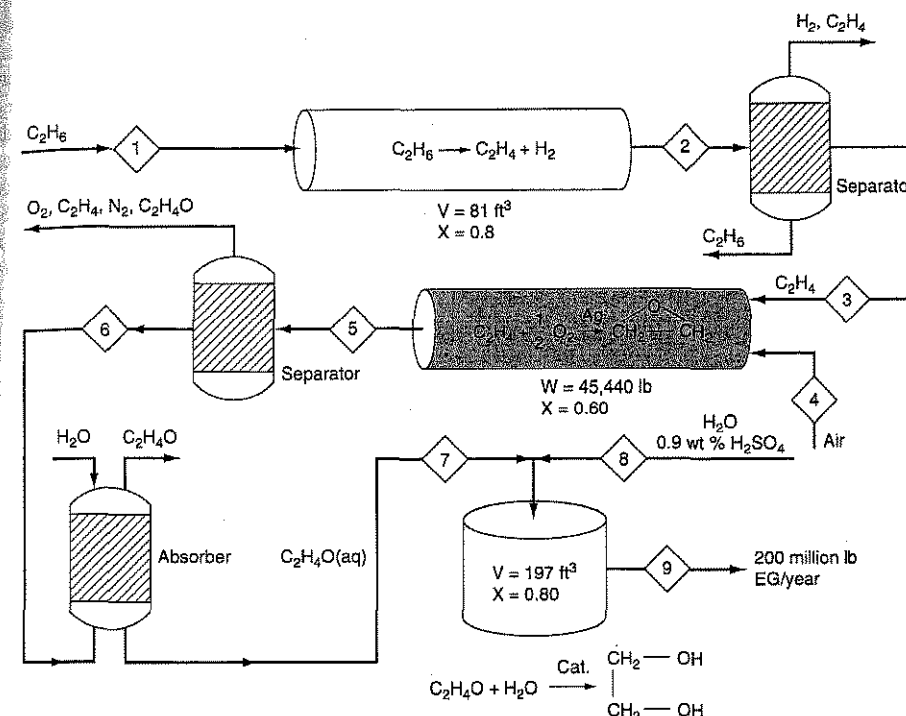
For the flow conditions given in Example 4-4 in a 1000-ft length of 1½-in. schedule 40 pipe ($\alpha_p = 0.0118$), the pressure drop is less than 10%.

4.5 Synthesizing a Chemical Plant

Careful study of the various reactions, reactors, and molar flows of the reactants and products used in the example problems in this chapter reveals that they can be arranged to form a chemical plant to produce 200 million pounds of ethylene glycol from a feedstock of 402 million pounds per year of ethane. The flowsheet for the arrangement of the reactors together with the molar flow rates is shown in Figure 4-11. Here 0.425 lb mol/s of ethane is fed to 100 tubular plug-flow reactors connected in parallel; the total volume is 81 ft³ to produce 0.34 lb mol/s of ethylene (see Example 4-4). The reaction mixture is then fed to a separation unit where 0.04 lb mol/s of ethylene is lost in the separation process in the ethane and hydrogen streams that exit the separator. This process provides a molar flow rate of ethylene of 0.3 lb mol/s which enters the packed-bed catalytic reactor together with 0.15 lb mol/s of O₂ and 0.564 lb mol/s of N₂. There are 0.18 lb mol/s of ethylene oxide (see Example 4-6) produced in the 1000 pipes arranged in parallel and packed with silver-coated catalyst pellets. There is 60% conversion achieved in each pipe and the total catalyst weight in all the pipes is 45,400 lb. The effluent stream is passed to a separator where 0.03 lb mol/s of ethylene oxide is lost. The ethylene oxide stream is then contacted with water in a gas absorber to produce a 1-lb mol/ft³ solution of ethylene oxide in water. In the absorption process, 0.022 lb mol/s of ethylene oxide is lost. The ethylene oxide solution is fed to a 197-ft³ CSTR together with a stream of 0.5 wt % H₂SO₄ solution to produce ethylene glycol

Synthesizing a chemical plant

Always challenge the assumptions, constraints, and boundaries of the problem



Stream	Component ^a	Flow rate (lb mol/s)	Stream	Component ^a	Flow rate (lb mol/s)
1	C ₂ H ₆	0.425	6	EO	0.150
2	C ₂ H ₄	0.340	7	EO	0.128
3	C ₂ H ₄	0.300	8	H ₂ O	0.44
4	Air	0.714	9	EG	0.104
5	EO	0.180			

^aEG, ethylene glycol; EO, ethylene oxide.

Figure 4-11 Production of ethylene glycol.

at a rate of 0.102 lb mol/s (see Example 4-2). This rate is equivalent to approximately 200 million pounds of ethylene glycol per year.

The profit from a chemical plant will be the difference between income from sales and the cost to produce the chemicals. An approximate formula might be

\$\$\$\$

$$\text{Profit} = \text{value of products} - \text{cost of reactants} \\ - \text{operating costs} - \text{separation costs}$$

The operating costs include such costs as energy, labor, overhead, and depreciation of equipment. You will learn more about these costs in your senior design course. While most if not all of the streams from the separators could be recycled, let's consider what the profit might be if the streams were to go unrecovered. Also, let's conservatively estimate the operating and other expenses to be \$8 million per year and calculate the profit. Your design instructor might give you a better number. The prices of ethane, sulfuric acid, and ethylene glycol are \$0.04, \$0.043, and \$0.38 per pound, respectively. See "http://www.chemweek.com/" for current prices.

For a feed of 4 million pounds per year and a production rate of 2 million pounds of ethylene glycol per year:

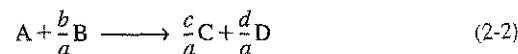
$$\begin{aligned} \text{profit} &= \frac{(\text{Ethylene Glycol Cost})}{\left(\frac{\$0.38}{\text{lb}} \times 2 \times 10^6 \frac{\text{lb}}{\text{year}} \right)} - \frac{(\text{Ethane Cost})}{\left(\frac{\$0.34}{\text{lb}} \times 4 \times 10^6 \frac{\text{lb}}{\text{year}} \right)} \\ &\quad - \frac{(\text{Sulfuric Acid Cost})}{\left(\frac{\$0.043}{\text{lb}} \times 2.26 \times 10^6 \frac{\text{lb}}{\text{year}} \right)} - \frac{\text{Operating Cost}}{\$8,000,000} \\ &= \$76,000,000 - \$16,000,000 - \$54,000 - \$8,000,000 \\ &\approx \$52 \text{ million} \end{aligned}$$

Using \$52 million a year as a rough estimate of the profit, you can now make different approximations about the conversion, separations, recycle streams, and operating costs to learn how they affect the profit.

4.6 Using C_A (liquid) and F_A (gas) in the Mole Balances and Rate Laws

Used for:
• Multiple rxns
• Membranes
• Unsteady state

There are a number of instances when it is much more convenient to work in terms of the number of moles (N_A , N_B) or molar flow rates (F_A , F_B , etc.) rather than conversion. Membrane reactors and multiple reactions taking place in the gas phase are two such cases where molar flow rates rather than conversion are preferred. In Section 3.4 we described how we can express concentrations in terms of the molar flow rates of the reacting species rather than conversion. We will develop our algorithm using concentrations (liquids) and molar flow rates (gas) as our dependent variables. The main difference is that when conversion is used as our variable to relate one species concentration to that of another species concentration, we needed to write a mole balance on only one species, our basis of calculation. When molar flow rates and concentrations are used as our variables, we must write a mole balance on each species and then relate the mole balances to one another through the relative rates of reaction; for



we have

$$\frac{r_A}{-a} = \frac{r_B}{-b} = \frac{r_C}{c} = \frac{r_D}{d} \quad (2-20)$$

Reaction (2-2) will be used together with the generic rate law

$$-r_A = k_A C_A^\alpha C_B^\beta \quad (5-2)$$

to develop the algorithms when C_i (liquids) and F_i (gases) are used as the system variables.

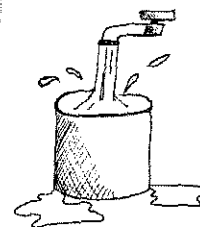
4.6.1 CSTRs, PFRs, PBRs, and Batch Reactors

Liquid Phase. For liquid-phase reactions in which there is no volume change, concentration is the preferred variable. The mole balances are shown in Table 4-5 in terms of concentration for the four reactor types we have been discussing. We see from Table 4-5 that we have only to specify the parameter values for the system (C_{A0} , v_0 , etc.) and for the rate law (i.e., k_A , α , β) to solve the coupled ordinary differential equations for either PFR, PBR, or batch reactors or to solve the coupled algebraic equations for a CSTR.

TABLE 4-5. MOLE BALANCES FOR LIQUID-PHASE REACTIONS

Batch	$\frac{dC_A}{dt} = r_A$	and	$\frac{dC_B}{dt} = \frac{b}{a}r_A$
CSTR	$V = \frac{v_0(C_{A0} - C_A)}{-r_A}$	and	$V = \frac{v_0(C_{B0} - C_B)}{-(b/a)r_A}$
PFR	$v_0 \frac{dC_A}{dV} = r_A$	and	$v_0 \frac{dC_B}{dV} = \frac{b}{a}r_A$
PBR	$v_0 \frac{dC_A}{dW} = r'_A$	and	$v_0 \frac{dC_B}{dW} = \frac{b}{a}r'_A$

LIQUIDS



Gas Phase. For gas-phase reactions, the mole balances are given identically in Table 4-6. Consequently, the concentrations in the rate laws need to be expressed in terms of the molar flow rates: for example,

$$r_j = kC_j^2$$

Rate law We start by recalling and combining Equations (3-40) and (3-41),

$$C_{T0} = \frac{F_{T0}}{v_0} = \frac{P_0}{Z_0 RT_0} \quad (3-40)$$

Stoichiometry

$$v = \left(\frac{v_0}{F_{T0}} \right) F_T \frac{P_0}{P} \frac{T}{T_0} \quad (3-41)$$

to give the case of an ideal gas ($Z = 1$). We now recall Equation (3-45),

$$C_j = C_{T0} \frac{F_j}{F_T} \frac{P}{P_0} \frac{T_0}{T} \quad (3-45)$$

The total molar flow rate is given as the sum of the flow rates of the individual species:

$$F_T = \sum_{j=1}^n F_j$$

when species A, B, C, D, and I are the only ones present. Then

$$F_T = F_A + F_B + F_C + F_D + F_I$$

The molar flow rates for each species F_j are obtained from a mole balance on each species, as given in Table 4-6: for example,

$$\frac{dF_j}{dV} = r_j \quad (4-42)$$

Must write a mole balance on each species

We now return to Example 3-8 to complete its solution.

TABLE 4-6. ALGORITHM FOR GAS-PHASE REACTIONS

$aA + bB \longrightarrow cC + dD$

1. Mole balances:

Batch	CSTR	PFR
$\frac{dN_A}{dt} = r_A V$	$V = \frac{F_{A0} - F_A}{-r_A}$	$\frac{dF_A}{dV} = r_A$
$\frac{dN_B}{dt} = r_B V$	$V = \frac{F_{B0} - F_B}{-r_B}$	$\frac{dF_B}{dV} = r_B$
$\frac{dN_C}{dt} = r_C V$	$V = \frac{F_{C0} - F_C}{-r_C}$	$\frac{dF_C}{dV} = r_C$
$\frac{dN_D}{dt} = r_D V$	$V = \frac{F_{D0} - F_D}{-r_D}$	$\frac{dF_D}{dV} = r_D$

2. Rate Law:

$$-r_A = k_A C_A^\alpha C_B^\beta$$

3. Stoichiometry:

Relative rates of reaction:

$$\frac{r_A}{-a} = \frac{r_B}{-b} = \frac{r_C}{c} = \frac{r_D}{d}$$

TABLE 4-6. (continued)

then

$$r_B = \frac{b}{a} r_A \quad r_C = -\frac{c}{a} r_A \quad r_D = -\frac{d}{a} r_A$$

Concentrations:

$$C_A = C_{T0} \frac{F_A}{F_T} \frac{P}{P_0} \frac{T_0}{T} \quad C_B = C_{T0} \frac{F_B}{F_T} \frac{P}{P_0} \frac{T_0}{T}$$

$$C_C = C_{T0} \frac{F_C}{F_T} \frac{P}{P_0} \frac{T_0}{T} \quad C_D = C_{T0} \frac{F_D}{F_T} \frac{P}{P_0} \frac{T_0}{T}$$

Total molar flow rate: $F_T = F_A + F_B + F_C + F_D$

4. Combine: For an isothermal operation of a PBR with no ΔP

$$\frac{dF_A}{dV} = -k_A C_{T0}^{\alpha+\beta} \left(\frac{F_A}{F_T} \right)^\alpha \left(\frac{F_B}{F_T} \right)^\beta \quad \frac{dF_{BC}}{dV} = -\frac{b}{a} k_A C_{T0}^{\alpha+\beta} \left(\frac{F_A}{F_T} \right)^\alpha \left(\frac{F_B}{F_T} \right)^\beta$$

$$\frac{dF_C}{dV} = \frac{c}{a} k_A C_{T0}^{\alpha+\beta} \left(\frac{F_A}{F_T} \right)^\alpha \left(\frac{F_B}{F_T} \right)^\beta \quad \frac{dF_{DC}}{dV} = \frac{d}{a} k_A C_{T0}^{\alpha+\beta} \left(\frac{F_A}{F_T} \right)^\alpha \left(\frac{F_B}{F_T} \right)^\beta$$

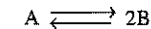
1. Specify parameter values: $k_A, C_{T0}, \alpha, \beta, T_0, a, b, c, d$

2. Specify entering numbers: $F_{A0}, F_{B0}, F_{C0}, F_{D0}$ and final values: V_{final}

5. Use an ODE solver.

Example 4-9 Working in Terms of Molar Flow Rates in a PFR

The gas-phase reaction



is carried out isothermally ($T = 500 \text{ K}$) and isobarically ($P_0 = 4.1 \text{ atm}$) in a PFR and follows an elementary rate law. Express the rate law and mole balances in terms of the molar flow rates and solve the combined equations to determine the molar flow rates along the length of a 100-dm³ PFR.

Additional information:

$$k_A = 2.7 \text{ min}^{-1}, K_C = 1.2 \text{ mol/dm}^3, F_{A0} = 10 \text{ mol/min}$$

Solution

Mole balance: $\frac{dF_A}{dV} = r_A \quad (\text{E4-9.1})$

$$\frac{dF_B}{dV} = r_B \quad (\text{E4-9.2})$$

Rate law: $-r_A = k_A \left(C_A - \frac{C_B^2}{K_C} \right) \quad (\text{E4-9.3})$

The algorithm

Stoichiometry. Using Equation (3-45) to substitute for the concentrations of A and B in terms of the molar flow rates, we have for $T = T_0$ and $P = P_0$ gives

$$C_A = C_{T0} \frac{F_A}{F_T} \quad (\text{E4-9.4})$$

$$C_B = C_{T0} \frac{F_B}{F_T} \quad (\text{E4-9.5})$$

where the total molar flow rate, F_T , is just the sum of the flow rates of A and B:

$$F_T = F_A + F_B \quad (\text{E4-9.6})$$

For every 1 mol of A disappearing 2 mol of B appear:

$$r_B = 2(-r_A) \quad (\text{E4-9.7})$$

and

$$F_B = 2(F_{A0} - F_A) \quad (\text{E4-9.8})$$

The total molar flow rate

$$F_T = F_A + 2F_{A0} - 2F_A = 2F_{A0} - F_A \quad (\text{E4-9.9})$$

and the total concentration at the entrance to the reactor (P_0 , T_0) is calculated from the equation

$$C_{T0} = \frac{P_0}{RT_0} = \frac{4.1 \text{ atm}}{0.082 \frac{\text{dm}^3 \cdot \text{atm}}{\text{mol} \cdot \text{K}} (500 \text{ K})} = 0.1 \frac{\text{mol}}{\text{dm}^3} \quad (\text{E4-9.10})$$

$$C_A = C_{T0} \frac{F_A}{2F_{A0} - F_A} \quad (\text{E4-9.11})$$

$$C_B = C_{T0} \frac{F_B}{2F_{A0} - F_A} \quad (\text{E4-9.12})$$

TABLE E4-9.1. POLYMATH PROGRAM

Equations	Initial Values
$d(f_A)/d(v) = r_A$	10
$ka = 2.7$	
$kc = 1.2$	
$ct0 = 0.1$	
$fa0 = 10$	
$fb = 2 * (fa0 - fa)$	
$ft = 2 * fa0 - fa$	
$ca = ct0 * fa / ft$	
$cb = ct0 * fb / ft$	
$ra = -ka * (ca - cb ** 2 / kc)$	
$rb = -2 * ra$	
$v_0 = 0, \quad v_f = 100$	

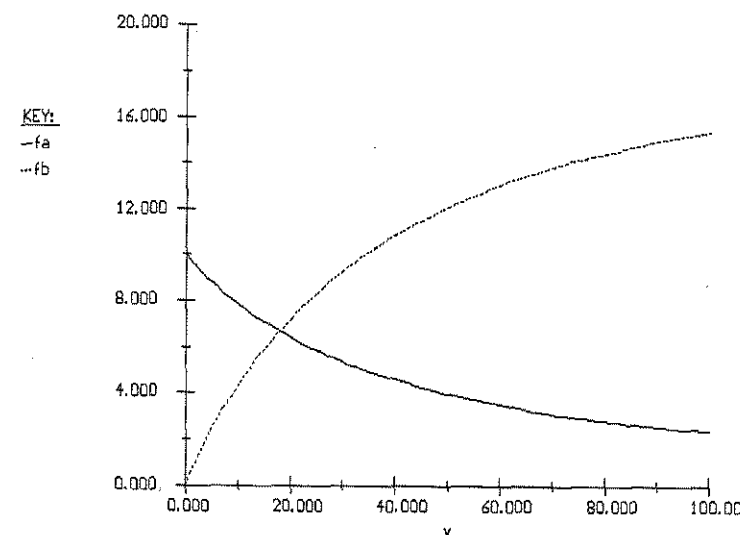


Figure E4-9.1 Molar flow rate profiles.

The mole balance (E4-9.1) and the rate laws (E4-9.3) are combined to give

$$\frac{dF_A}{dV} = r_A = -k_A[C_A - C_B^2/K_C] \quad (\text{E4-9.13})$$

Equations (E4-9.11) through (E4-9.13) can now be solved numerically, preferably by a software package such as POLYMATH or MATLAB. The POLYMATH program and solution are given in Table E4-9.1 for $k_A = 2.7 \text{ min}^{-1}$, $K_C = 1.2 \text{ mol/dm}^3$, and $F_{A0} = 10 \text{ mol/min}$. The MATLAB program is included on the CD-ROM.

The molar flows of A and B at equilibrium can be found as follows:

$$K_C = \frac{C_{B_e}^2}{C_{A_e}} = \frac{\left[C_{T0} \left(\frac{F_{B_e}}{F_{A_e} + F_{B_e}} \right) \right]^2}{C_{T0} \left(\frac{F_{A_e}}{F_{A_e} + F_{B_e}} \right)} \quad (\text{E4-9.14})$$

simplifying

$$\frac{C_{T0} F_{B_e}^2}{F_{A_e} (F_{A_e} + F_{B_e})} = K_C \quad (\text{E4-9.15})$$

Substituting for F_{B_e} , C_{T0} , and K_C gives

$$\frac{(0.1)(2)^2(10 - F_{A_e})^2}{F_{A_e}(2F_{A0} - F_{A_e})} = 1.2 \quad (\text{E4-9.16})$$

Equations (E4-9.15) and (E4-9.16) solve to

$$F_{Ae} = 1.34 \text{ mol/min}$$

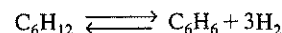
$$F_{Be} = 17.32 \text{ mol/min}$$

We note from Figure E4-9.1 that the molar flow rates begin to approach the equilibrium values near the end of the reactor.

4.6.2 Membrane Reactors

Catalytic membrane reactors can be used to increase the yield of reactions that are highly reversible over the temperature range of interest. (Some refer to this type of reaction as being thermodynamically limited.) The term *membrane reactor* describes a number of different types of reactor configurations that contain a membrane. The membrane can either provide a barrier to certain components, while being permeable to others, prevent certain components such as particulates from contacting the catalyst, or contain reactive sites and be a catalyst in itself. Like reactive distillation, the membrane reactor is another technique for driving reversible reactions to the right in order to achieve very high conversions. These high conversions can be achieved by having one of the reaction products diffuse out of a semipermeable membrane surrounding the reacting mixture.⁵ As a result, the reaction will continue to proceed to the right toward completion.

Two of the main types of catalytic membrane reactors are shown in Figure 4-12. The reactor in the middle is called an *inert membrane reactor with catalyst pellets on the feed side* (IMRCF). Here the membrane is inert and serves as a barrier to the reactants and some of the products. The reactor on the bottom is a *catalytic membrane reactor* (CMR). The catalyst is deposited directly on the membrane and only specific reaction products are able to exit the permeate side. For example, in the reversible reaction



the hydrogen molecule is small enough to diffuse through the small pores of the membrane while C_6H_{12} and C_6H_6 cannot. Consequently, the reaction continues to proceed to the right even for a small value of the equilibrium constant.

Detailed modeling of the transport and reaction steps in membrane reactors is beyond the scope of this text but can be found in *Membrane Reactor Technology*.⁶ The salient features, however, can be illustrated by the following example. When analyzing membrane reactors, it is much more convenient to use molar flow rates rather than conversion.

⁵ R. Govind, and N. Itoh, eds., *Membrane Reactor Technology*, AIChE Symposium Series No. 268, Vol. 85 (1989). T. Sun and S. Khang, *Ind. Eng. Chem. Res.*, 27, 1136 (1988).

⁶ Govind and Itoh, *Membrane Reactor Technology*.

By having one of the products pass throughout the membrane, we drive the reaction towards completion

H_2 diffuses through the membrane while C_6H_6 does not

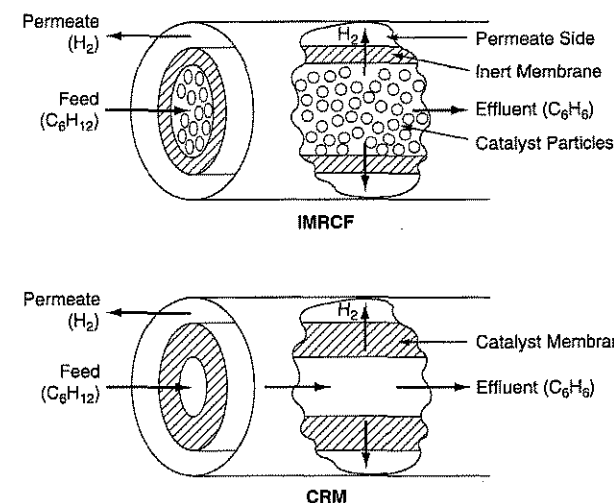
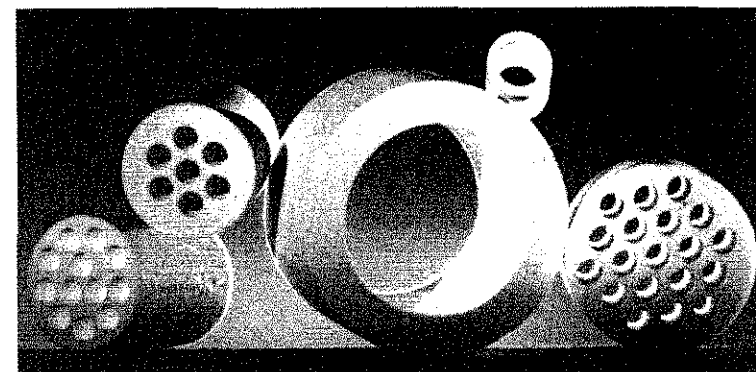
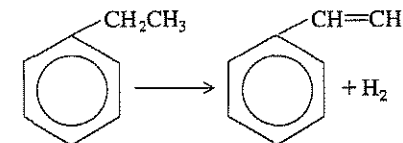


Figure 4-12 Membrane reactors. (Photo courtesy of Coors Ceramics, Golden, Colorado.)

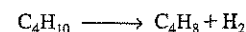
According to the DOE, 10 trillion BTU/yr could be saved by using membrane reactors

Example 4-10 Membrane Reactor

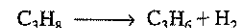
According to The Department of Energy, an energy saving of 10 trillion Btu per year could result from the use of catalytic membrane reactors as replacements for conventional reactors for dehydrogenation reactions such as the dehydrogenation of ethylbenzene to styrene:



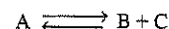
and of butane to butene:



The dehydrogenation of propane is another reaction that has proven successful with a membrane reactor [J. Membrane Sci., 77, 221 (1993)].



All the dehydrogenation reactions above can be represented symbolically as



and will take place on the catalyst side of an IMRCF. The equilibrium constant for this reaction is quite small at 227°C (i.e., $K_C = 0.05 \text{ mol/dm}^3$). The membrane is permeable to B (e.g. H_2) but not to A and C. Pure gaseous A enters the reactor at 8.2 atm and 227°C at a rate of 10 mol/min.

As a first approximation assume that the rate of diffusion of B out of the reactor per unit volume of reactor, R_B , is taken to be proportional to the concentration of B (i.e., $R_B = k_c C_B$).

(a) Perform differential mole balances on A, B, and C to arrive at a set of coupled differential equations to solve.

(b) Plot the molar flow rates of each species as a function of space time.

Additional information: Even though this reaction is a gas-solid catalytic reaction, we will make use of the bulk catalyst density in order to write our balances in terms of reactor volume rather than catalyst weight (recall $-r_A = -r'_A \rho_b$). For the bulk catalyst density of $\rho_b = 1.5 \text{ g/cm}^3$ and a 2-cm inside diameter of the tube containing the catalyst pellets, the specific reaction rate, k , and the transport coefficient, k_c , are $k = 0.7 \text{ min}^{-1}$ and $k_c = 0.2 \text{ min}^{-1}$, respectively.

Solution

We shall choose reactor volume rather than catalyst weight as our independent variable for this example. First we shall perform mole balances on the volume element ΔV shown in Figure E4-10.1.

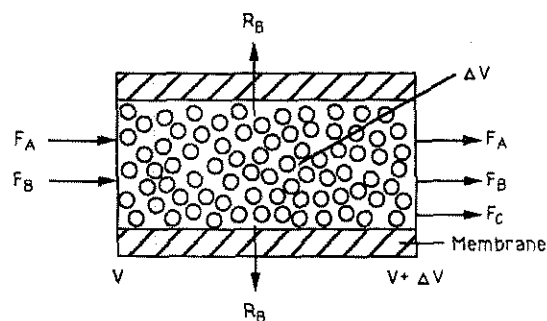


Figure E4-10.1

1. Mole balances:

Balance on A in the catalytic bed:

$$\left[\begin{array}{c} \text{In} \\ \text{by Flow} \end{array} \right] - \left[\begin{array}{c} \text{Out} \\ \text{by Flow} \end{array} \right] + \left[\begin{array}{c} \text{Generation} \end{array} \right] = \left[\begin{array}{c} \text{Accumulation} \end{array} \right]$$

$$F_A|_V - F_A|_{V+\Delta V} + r_A \Delta V = 0$$

Dividing by ΔV and taking the limit as $\Delta V \rightarrow 0$ gives

$$\boxed{\frac{dF_A}{dV} = r_A} \quad (\text{E4-10.1})$$

Balance on B in the catalytic bed:

$$\left[\begin{array}{c} \text{In} \\ \text{by Flow} \end{array} \right] - \left[\begin{array}{c} \text{Out} \\ \text{by Flow} \end{array} \right] - \left[\begin{array}{c} \text{Out} \\ \text{by Diffusion} \end{array} \right] + \left[\begin{array}{c} \text{Generation} \end{array} \right] = \left[\begin{array}{c} \text{Accumulation} \end{array} \right]$$

$$F_B|_V - F_B|_{V+\Delta V} - R_B \Delta V + r_B \Delta V = 0$$

where R_B is the molar flow of B out through the membrane per unit volume of reactor. Dividing by ΔV and taking the limit as $\Delta V \rightarrow 0$ gives

$$\boxed{\frac{dF_B}{dV} = r_B - R_B} \quad (\text{E4-10.2})$$

The mole balance on C is carried out in an identical manner to A and the resulting equation is

$$\frac{dF_C}{dV} = r_C \quad (\text{E4-10.3})$$

2. Rate law:

$$\boxed{-r_A = k \left(C_A - \frac{C_B C_C}{K_C} \right)} \quad (\text{E4-10.4})$$

$$r_B = -r_A$$

$$r_C = -r_A$$

3. Transport out the sides of the reactor. We have assumed that

$$\boxed{R_B = k_c C_B} \quad (\text{E4-10.5})$$

where k_c is a transport coefficient. In general, this coefficient can be a function of the membrane and fluid properties, the fluid velocity, the tube diameter, and so on (see Chapter 11). However, in this example we assume that the main resistance to diffusion of B out of the reactor is the membrane itself and consequently, k_c is taken to be a constant.

Note there are two "OUT" terms for species B

4. **Stoichiometry.** Recalling Equation (3-45) for the case of constant temperature and pressure, we have for isothermal operation and no pressure drop ($T = T_0$, $P = P_0$),

$$C_A = C_{T0} \frac{F_A}{F_T} \quad (\text{E4-10.6})$$

$$C_B = C_{T0} \frac{F_B}{F_T} \quad (\text{E4-10.7})$$

$$C_C = C_{T0} \frac{F_C}{F_T} \quad (\text{E4-10.8})$$

$$F_T = F_A + F_B + F_C \quad (\text{E4-10.9})$$

$$-r_A = r_B = r_C \quad (\text{E4-10.10})$$

5. Combining and summarizing:

$$\begin{aligned} \frac{dF_A}{dV} &= r_A \\ \frac{dF_B}{dV} &= -r_A - k_c C_{T0} \left(\frac{F_B}{F_T} \right) \\ \frac{dF_C}{dV} &= -r_A \\ -r_A &= k C_{T0} \left[\left(\frac{F_A}{F_T} \right) - \frac{C_{T0}}{K_C} \left(\frac{F_B}{F_T} \right) \left(\frac{F_C}{F_T} \right) \right] \\ F_T &= F_A + F_B + F_C \end{aligned}$$

Summary of equations describing flow and reaction in a membrane reactor

6. Parameter evaluation:

$$C_{T0} = \frac{P_0}{RT_0} = \frac{8.2 \text{ atm}}{0.082 \text{ atm} \cdot \text{dm}^3 / (\text{mol} \cdot \text{K}) (500 \text{ K})} = 0.2 \frac{\text{mol}}{\text{dm}^3}$$

$$k = 0.7 \text{ min}^{-1}, K_C = 0.05 \text{ mol/dm}^3, k_c = 0.2 \text{ min}^{-1}$$

$$F_{A0} = 10 \text{ mol/min}$$

$$F_{B0} = F_{C0} = 0$$

7. **Numerical solution.** Equations (E4-10.1) through (E4-10.10) were solved using POLYMATH and another ODE Solver MATLAB. The profiles of the molar flow rates are shown below. Table E4-10.1 shows the POLYMATH

programs, and Figure E4-10.2 shows the results of the numerical solution of the initial (entering) conditions.

$$A = 0 \quad F_A = F_{A0} \quad F_B = 0 \quad F_C = 0$$

TABLE E4-10.1. POLYMATH PROGRAM

Equations	Initial Values
$d(F_B)/d(V) = -r_A - k_c C_{T0} (F_B/F_T)$	0
$d(F_A)/d(V) = r_A$	1.0
$d(F_C)/d(V) = -r_A$	0
$k_c = 0.2$	
$C_{T0} = 0.2$	
$F_T = F_A + F_B + F_C$	
$k = 0.7$	
$K_C = 0.05$	
$r_A = -k C_{T0} \left\{ \left(\frac{F_A}{F_T} \right) - \frac{C_{T0}}{K_C} \left(\frac{F_B}{F_T} \right) \left(\frac{F_C}{F_T} \right) \right\}$	
$V_0 = 0, \quad V_f = 500$	

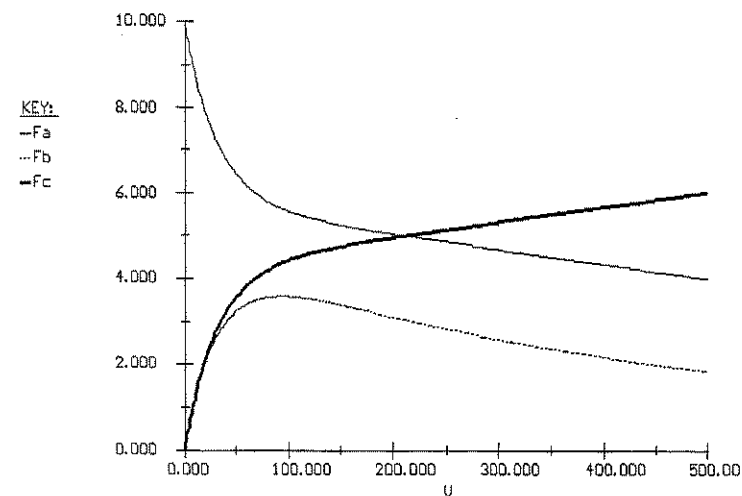


Figure E4-10.2 POLYMATH solution.

4.7 Unsteady-State Operation of Reactors

In this chapter we have already discussed the unsteady operation of one type of reactor, the batch reactor. In this section we discuss two other aspects of unsteady operation. First, the startup of a CSTR is examined to determine the

time necessary to reach steady-state operation (see Figure 4-13a). Next, semibatch reactors are discussed. In each of these cases, we are interested in predicting the concentration and conversion as a function of time. Closed-form analytical solutions to the differential equations arising from the mole balance of these reaction types can be obtained only for zero- and first-order reactions. ODE solvers must be used for other orders.

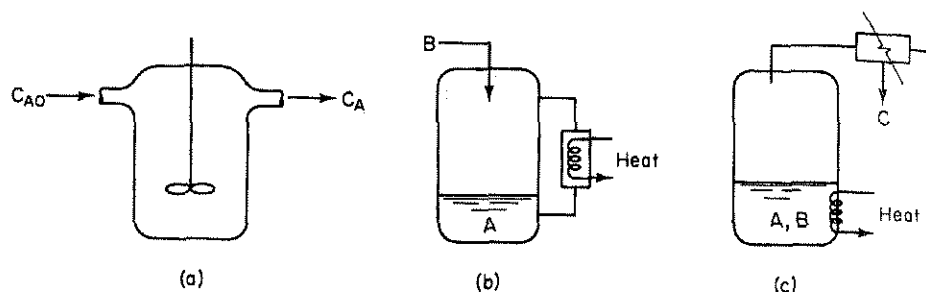
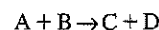


Figure 4-13 Semibatch reactors. [Excerpted by special permission from *Chem. Eng.*, 63(10) 211 (Oct. 1956). Copyright © 1956 by McGraw-Hill, Inc., New York, NY 10020.]

There are two basic types of semibatch operations. In one type, one of the reactants in the reaction



(e.g., B) is slowly fed to a reactor containing the other reactant (e.g., A), which has already been charged to a reactor such as that shown in Figure 4-13b. This type of reactor is generally used when unwanted side reactions occur at high concentrations of B, or the reaction is highly exothermic. In some reactions, the reactant B is a gas and is bubbled continuously through liquid reactant A. Examples of reactions used in this type of semibatch reactor operation include *ammonolysis*, *chlorination*, and *hydrolysis*. The other type of semibatch reactor is shown schematically in Figure 4-13c. Here reactants A and B are charged simultaneously and one of the products is vaporized and withdrawn continuously. Removal of one of the products in this manner (e.g., C) shifts the equilibrium towards the right, increasing the final conversion above that which would be achieved had C not been removed. In addition, removal of one of the products further concentrates the reactant, thereby producing an increased rate of reaction and decreased processing time. This type of reaction operation is called *reactive distillation*. Examples of reactions carried out in this type of reactor include *acetylation reactions* and *esterification reactions* in which water is removed.

4.7.1 Startup of a CSTR

The startup of a fixed volume CSTR under isothermal conditions is rare, but it does occur occasionally. Here we want to determine the time necessary to reach steady-state operation. We begin with the general mole balance equation applied to Figure 4-13a:

$$F_{A0} - F_A + r_A V = \frac{dN_A}{dt} \quad (4-43)$$

Conversion does not have any meaning in startup because one cannot separate the moles reacted from the moles accumulated in the CSTR. Consequently, we must use concentration rather than conversion as our variable in the balance equation. For liquid-phase ($v = v_0$) reactions with constant overflow ($V = V_0$), using $\tau = V_0/v_0$ we can transform Equation (4-43) to

$$C_{A0} - C_A + r_A \tau = \tau \frac{dC_A}{dt} \quad (4-44)$$

For a first-order reaction ($-r_A = kC_A$) Equation (4-44) then becomes

$$\frac{dC_A}{dt} + \frac{1 + \tau k}{\tau} C_A = \frac{C_{A0}}{\tau} \quad (4-45)$$

which solves to

$$C_A = \frac{C_{A0}}{1 + \tau k} \left\{ 1 - \exp \left[-(1 + \tau k) \frac{t}{\tau} \right] \right\} \quad (4-46)$$

Letting t_s be the time necessary to reach 99% of the steady-state concentration, C_{As} :

$$C_{As} = \frac{C_{A0}}{1 + \tau k} \quad (4-47)$$

Rearranging Equation (4-46) for $C_A = 0.99C_{As}$ yields

$$t_s = 4.6 \frac{\tau}{1 + \tau k} \quad (4-48)$$

For slow reactions:

$$t_s = 4.6 \tau \quad (4-49)$$

For rapid reactions:

$$t_s = \frac{4.6}{k} \quad (4-50)$$

For most first-order systems, steady state is achieved in three to four space times.

An expanded version of this section can be found on the CD-ROM



Time to reach steady state in an isothermal CSTR

4.7.2 Semibatch Reactors

Of the two types of semibatch reactors described earlier, we focus attention primarily on the one with constant molar feed. A schematic diagram of this semibatch reactor is shown in Figure 4-14. We shall consider the elementary liquid-phase reaction

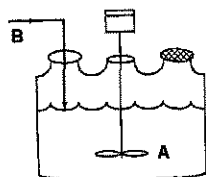
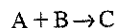


Figure 4-14 Semibatch reactor.

in which reactant B is slowly added to a vat containing reactant A. A mole balance on species A yields

$$\left[\begin{array}{c} \text{rate} \\ \text{in} \end{array} \right] - \left[\begin{array}{c} \text{rate} \\ \text{out} \end{array} \right] + \left[\begin{array}{c} \text{rate of} \\ \text{generation} \end{array} \right] = \left[\begin{array}{c} \text{rate of} \\ \text{accumulation} \end{array} \right] \quad (4-51)$$

$$0 - 0 + r_A V(t) = \frac{dN_A}{dt}$$

There are three variables that can be used to formulate and solve semibatch reactor problems: the concentration, C_j , the number of moles, N_j , and the conversion, X .

Writing the Semibatch Reactor Equations in Terms of Concentrations. Recalling that the number of moles of A is just the product of concentration of A, C_A , and the volume V , we can rewrite Equation (4-51) as

$$r_A V = \frac{d(C_A V)}{dt} = \frac{V dC_A}{dt} + C_A \frac{dV}{dt} \quad (4-52)$$

We note that since the reactor is being filled, the volume, V , varies with time. The reactor volume at any time t can be found from an overall mass balance of all species:

$$\left[\begin{array}{c} \text{rate} \\ \text{in} \end{array} \right] - \left[\begin{array}{c} \text{rate} \\ \text{out} \end{array} \right] + \left[\begin{array}{c} \text{rate of} \\ \text{generation} \end{array} \right] = \left[\begin{array}{c} \text{rate of} \\ \text{accumulation} \end{array} \right] \quad (4-53)$$

$$\rho_0 v_0 - 0 + 0 = \frac{d(\rho V)}{dt}$$

For a constant-density system, $\rho_0 = \rho$, and

$$\frac{dV}{dt} = v_0 \quad (4-54)$$

with the initial condition $V = V_0$ at $t = 0$, integrating for the case of constant V_0 yields

$$V = V_0 + v_0 t \quad (4-55)$$

Substituting Equation (4-54) into the right-hand side of Equation (4-52) and rearranging gives us

$$-v_0 C_A + V r_A = \frac{V dC_A}{dt}$$

The balance of A [i.e. Equation (4-52)] can be rewritten as

$$\frac{dC_A}{dt} = r_A - \frac{v_0}{V} C_A \quad (4-56)$$

A mole balance of B that is fed to the reactor at a rate F_{B0} is

$$\frac{dN_B}{dt} = r_B V + F_{B0} \quad (4-57)$$

$$\frac{dV C_B}{dt} = \frac{dV}{dt} C_B + \frac{V dC_B}{dt} = r_B V + F_{B0}$$

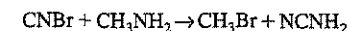
Substituting Equation (4-55) in terms of V and differentiating, the mole balance on B becomes

$$\frac{dC_B}{dt} = r_B + \frac{v_0(C_{B0} - C_B)}{V} \quad (4-58)$$

If the reaction order is other than zero- or first-order, or if the reaction is nonisothermal, we must use numerical techniques to determine the conversion as a function of time. Equations (4-56) and (4-58) are easily solved with an ODE solver.

Example 4-11 Isothermal Semibatch Reactor with Second-Order Reaction

The production of methyl bromide is an irreversible liquid-phase reaction that follows an elementary rate law. The reaction



is carried out isothermally in a semibatch reactor. An aqueous solution of methyl amine (B) at a concentration of 0.025 g mol/dm^3 is to be fed at a rate of $0.05 \text{ dm}^3/\text{s}$ to an aqueous solution of bromine cyanide (A) contained in a glass-lined reactor.

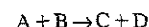
The initial volume of fluid in a vat is to be 5 dm³ with a bromine cyanide concentration of 0.05 mol/dm³. The specific reaction rate constant is

$$k = 2.2 \text{ dm}^3/\text{s} \cdot \text{mol}$$

Solve for the concentrations of bromine cyanide and methyl bromide and the rate of reaction as a function of time.

Solution

Symbolically, we write the reaction as



The reaction is elementary; therefore, the rate law is

Rate Law

$$-r_A = kC_A C_B \quad (\text{E4-11.1})$$

Substituting the rate law in Equations (4-56) and (4-58) gives

Mole balances on
A, B, C, and D

$$\frac{dC_A}{dt} = -kC_A C_B - \frac{v_0}{V} C_A \quad (\text{E4-11.2})$$

$$\frac{dC_B}{dt} = -kC_A C_B + \frac{v_0}{V} (C_{B0} - C_B) \quad (\text{E4-11.3})$$

$$V = V_0 + v_0 t \quad (\text{E4-11.4})$$

Similarly for C and D we have

$$\frac{dN_C}{dt} = r_C V = -r_A V \quad (\text{E4-11.5})$$

$$\frac{dN_C}{dt} = \frac{d(C_C V)}{dt} = V \frac{dC_C}{dt} + C_C \frac{dV}{dt} = V \frac{dC_C}{dt} + v_0 C_C \quad (\text{E4-11.6})$$

Then

$$\frac{dC_C}{dt} = kC_A C_B - \frac{v_0 C_C}{V} \quad (\text{E4-11.7})$$

and

$$\frac{dC_D}{dt} = kC_A C_B - \frac{v_0 C_D}{V} \quad (\text{E4-11.8})$$

We could also calculate the conversion of A.

$$X = \frac{N_{A0} - N_A}{N_{A0}} \quad (\text{E4-11.9})$$

$$X = \frac{C_{A0} V_0 - C_A V}{C_{A0} V_0} \quad (\text{E4-11.10})$$

The initial conditions are $t = 0$, $C_A = 0.05$, $C_B = 0$, $C_C = C_D = 0$, and $V_0 = 5$.

Equations (E4-11.2) through (E4-11.10) are easily solved with the aid of an ODE solver such as POLYMATH (Table E4-11.1).

TABLE E4-11.1. POLYMATH PROGRAM

Equations	Initial Values
$d(ca)/d(t) = -k*ca*cb - v00*ca/v$	0.05
$d(cb)/d(t) = -k*ca*cb + v00*(cb0 - cb)/v$	0
$d(cc)/d(t) = k*ca*cb - v00*cc/v$	0
$d(cd)/d(t) = k*ca*cb - v00*cd/v$	0
$k = 2.2$	
$v00 = 0.05$	
$cb0 = 0.025$	
$v0 = 5$	
$ca0 = 0.05$	
$rate = k*ca*cb$	
$v = v0 + v00*t$	
$x = (ca0*v0 - ca*v)/(ca0*v0)$	
$t_0 = 0, \quad t_f = 500$	

The concentrations of bromine cyanide (A), and methyl amine are shown as a function of time in Figure E4-11.1, and the rate is shown in Figure E4-11.2. For first- and zero-order reactions we can obtain analytical solutions for semibatch reactors operated isothermally.

Why does the concentration of CH₃ Br go through a maximum w.r.t. time?

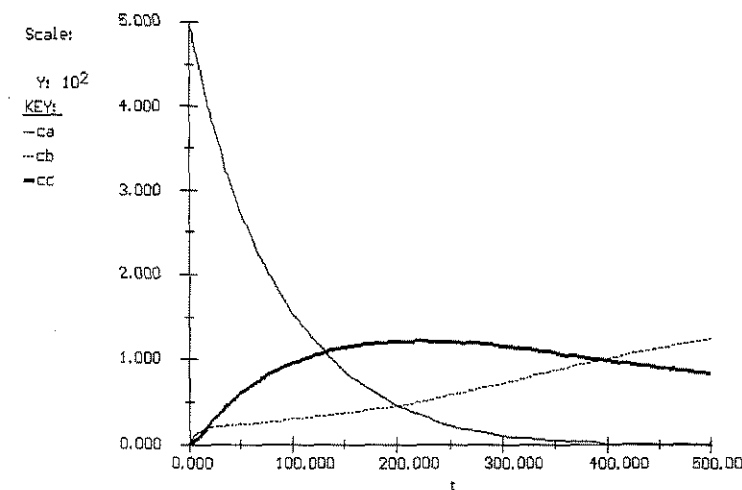


Figure E4-11.1 Concentration-time trajectories.

Why does the reaction rate go through a maximum?

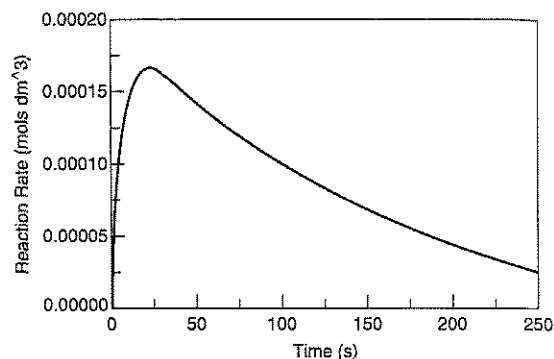


Figure E4-11.2 Reaction rate-time trajectory.

Writing the Semibatch Reactor Equations in Terms of the Number of Moles. We can also solve semibatch reactor problems by leaving the mole balance equations in terms of the number of moles of each species (i.e., N_A , N_B , N_C , and N_D).

Recalling the mole balance equations for A and B, Equations (4-51) and (4-57), respectively, along with the equation for the reactor volume, Equation (4-55), we have

$$\frac{dN_A}{dt} = r_A V(t) \quad (4-51)$$

$$\frac{dN_B}{dt} = r_A V(t) + F_{B0} \quad (4-57)$$

$$V = V_0 + v_0 t \quad (4-55)$$

One now recalls from Chapter 3 the definition of concentration for a batch system [Equation (3-24)]:

$$C_A = \frac{N_A}{V} \quad (3-24)$$

$$C_B = \frac{N_B}{V}$$

and substitutes these equations into the rate law to obtain equations that are stated solely in terms of the number of moles. For example, if $-r_A = k_A C_A C_B$, then

$$\frac{dN_A}{dt} = -k \frac{N_A N_B}{V_0 + v_0 t} \quad (4-59)$$

and

$$\frac{dN_B}{dt} = -k \frac{N_A N_B}{V_0 + v_0 t} + F_{B0} \quad (4-60)$$

One now has only to specify the parameter values (k , V_0 , v_0 , F_{B0}) and the initial conditions to solve these equations for N_A and N_B .

Writing the Semibatch Reactor Equations in Terms of Conversion. Consider the reaction



in which B is fed to a vat containing only A initially. The reaction is first-order in A and first-order in B. The number of moles of A remaining at any time, t , can be found from the balance,

$$\begin{aligned} \left[\begin{array}{c} \text{number of moles} \\ \text{of A in the vat} \\ \text{at time } t \end{array} \right] &= \left[\begin{array}{c} \text{number of moles} \\ \text{of A in the vat} \\ \text{initially} \end{array} \right] - \left[\begin{array}{c} \text{number of moles} \\ \text{of A reacted up} \\ \text{to time } t \end{array} \right] \quad (4-61) \\ N_A &= N_{A0} - N_{A0}X \end{aligned}$$

where X is the moles of A reacted per mole of A initially in the vat. Similarly, for species B,

$$\begin{aligned} \left[\begin{array}{c} \text{number of moles} \\ \text{of B in the vat} \\ \text{at time } t \end{array} \right] &= \left[\begin{array}{c} \text{number of moles} \\ \text{of B in the vat} \\ \text{initially} \end{array} \right] + \left[\begin{array}{c} \text{number of moles} \\ \text{of B added to} \\ \text{the vat} \end{array} \right] - \left[\begin{array}{c} \text{number of moles} \\ \text{of B reacted up} \\ \text{to time } t \end{array} \right] \\ N_B &= N_{B0} + \int_0^t F_{B0} dt - N_{A0}X \quad (4-62) \end{aligned}$$

For a constant molar feed rate

$$N_B = N_{B0} + F_{B0}t - N_{A0}X \quad (4-63)$$

A mole balance on species A gives

$$r_A V = \frac{dN_A}{dt} \quad (4-64)$$

The number of moles of C and D can be taken directly from the stoichiometric table; for example,

$$N_C = N_{C0} + N_{A0}X$$

For a reversible second-order reaction $A + B \rightleftharpoons C + D$ for which the rate law is

$$-r_A = k \left(C_A C_B - \frac{C_C C_D}{K_C} \right) \quad (4-65)$$

Concentration
of reactants as a
function of
conversion and
time

the concentrations of A and B are

$$C_A = \frac{N_A}{V} = \frac{N_{A0}(1-X)}{V_0 + v_0 t} \quad C_C = \frac{N_{A0}X}{V_0 + v_0 t}$$

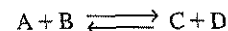
$$C_B = \frac{N_B}{V} = \frac{N_{B0} + F_{B0}t - N_{A0}X}{V_0 + v_0 t} \quad C_D = \frac{N_{A0}X}{V_0 + v_0 t}$$

Combining equations (4-61), (4-64), and (4-65), substituting for the concentrations and dividing by N_{A0} , we obtain

$$\frac{dX}{dt} = \frac{k[(1-X)(N_{B0} + F_{B0}t - N_{A0}X) - (N_{A0}X^2/K_C)]}{V_0 + v_0 t} \quad (4-66)$$

Equation (4-66) needs to be solved numerically to determine the conversion as a function of time.

Equilibrium Conversion. For reversible reactions carried out in a semibatch reactor, the maximum attainable conversion (i.e., the equilibrium conversion) will change as the reaction proceeds because more reactant is continuously added to the reactor. This addition shifts the equilibrium continually to the right. Consider the reversible reaction



for which the rate law is

$$-r_A = k \left(C_A C_B - \frac{C_C C_D}{K_C} \right) \quad (4-67)$$

If the reaction were allowed to reach equilibrium after feeding species B for a time t , the equilibrium conversion could be calculated as follows:

$$K_C = \frac{C_{Ce} C_{De}}{C_{Ae} C_{Be}} = \frac{\left(\frac{N_{Ce}}{V} \right) \left(\frac{N_{De}}{V} \right)}{\left(\frac{N_{Ae}}{V} \right) \left(\frac{N_{Be}}{V} \right)} \quad (3-10)$$

$$= \frac{N_{Ce} N_{De}}{N_{Ae} N_{Be}}$$

The relationship between conversion and number of moles of each species is the same as shown in Table 3-1 except for species B, for which the number of moles is given by Equation (4-63). Thus

$$K_C = \frac{(N_{A0}X_e)(N_{A0}X_e)}{N_{A0}(1-X_e)(F_{B0}t - N_{A0}X_e)} \quad (4-68)$$

$$= \frac{N_{A0}X_e^2}{(1-X_e)(F_{B0}t - N_{A0}X_e)}$$

Rearranging yields

$$t = \frac{N_{A0}}{K_C F_{B0}} \left(K_C X_e + \frac{X_e^2}{1-X_e} \right) \quad (4-69)$$

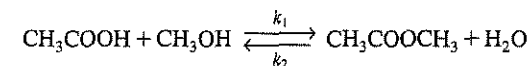
or

$$X_e = \frac{K_C \left(1 + \frac{F_{B0}t}{N_{A0}} \right) - \sqrt{\left[K_C \left(1 + \frac{F_{B0}t}{N_{A0}} \right) \right]^2 - 4(K_C - 1)K_C \frac{tF_{B0}}{N_{A0}}}}{2(K_C - 1)} \quad (4-70)$$

Equilibrium
conversion
in a semibatch
reactor

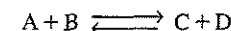
4.7.3 Reactive Distillation

The distillation of chemically reacting mixtures has become increasingly common in chemical industries.⁷ Carrying out these two operations, reaction and distillation, simultaneously in a single unit results in significantly lower capital and operating costs. Reactive distillation is particularly attractive when one of the reaction products has a lower boiling point, resulting in its volatilization from the reacting liquid mixture. An example of reactive distillation is the production of methyl acetate:



By continually removing the volatile reaction product, methyl acetate, from the reacting liquid-phase reaction, the reverse reaction is negligible and the reaction continues to proceed towards completion in the forward direction.

Although reactive distillation will not be treated in detail, it is worthwhile to set down the governing equations. We consider the elementary reaction



in which A and B are charged in equal molar amounts and species D is continuously boiled off. A balance on species A gives

$$0 - 0 + r_A V = \frac{dN_A}{dt} \quad (4-71)$$

⁷ H. Sawistowski and P. A. Pilavakis, *Chem. Eng. Sci.*, 43, 355 (1988).

If we define conversion as the number of moles of A reacted per mole of A charged, then

$$N_A = N_{A0}(1 - X) \quad (4-72)$$

and

$$N_B = N_{A0} \left(\Theta_B - \frac{b}{a} X \right) = N_{A0}(1 - X) \quad (4-73)$$

Substituting Equation (4-72) into (4-71) gives

$$N_{A0} \frac{dX}{dt} = -r_A V \quad (4-74)$$

A balance on species D, which evaporates at a rate F_D after being formed, gives

$$0 - F_D + r_D V = \frac{dN_D}{dt} \quad (4-75)$$

Integrating, we have

$$\left[\begin{array}{c} \text{number of moles} \\ \text{of remaining D} \end{array} \right] = \left[\begin{array}{c} \text{number of moles of D} \\ \text{formed by reaction} \end{array} \right] - \left[\begin{array}{c} \text{number of moles of D} \\ \text{lost by vaporization} \end{array} \right] \quad (4-76)$$

$$N_D = N_{A0}X - \int_0^t F_D dt$$

For the elementary reaction given,

$$-r_A = k \left(C_A C_B - \frac{C_C C_D}{K_C} \right)$$

$$C_A = \frac{N_{A0}(1 - X)}{V}$$

$$C_B = \frac{N_B}{V} = \frac{N_{A0}(1 - X)}{V}$$

$$C_C = \frac{N_C}{V} = \frac{N_{A0}X}{V}$$

$$C_D = \frac{N_D}{V} = \frac{N_{A0}X - \int_0^t F_D dt}{V}$$

$$-r_A V = \frac{k N_{A0}^2 \left[(1 - X)^2 - \frac{X}{K_C} \left(X - \frac{1}{N_{A0}} \int_0^t F_D dt \right) \right]}{V} \quad (4-77)$$

We now need to determine the volume as a function of either conversion or time. An overall mass balance on all species gives

$$0 - F_D(\text{MW}_D) + 0 = \frac{d(\rho V)}{dt} \quad (4-78)$$

where MW_D is the molecular weight of D. For a constant-density system,

$$\frac{dV}{dt} = -\frac{F_D(\text{MW}_D)}{\rho} = -\alpha F_D \quad (4-79)$$

This equation must now be solved numerically and simultaneously with equations (4-74) through (4-77). However, in order to solve the set of equations above we need to specify the rate of evaporation of D, F_D .

Case 1 Immediate Evaporation

For the case where D evaporates immediately after being formed, we can obtain an analytical solution. For no accumulation of D in the liquid phase,

$$F_D = r_D V = -r_A V \quad (4-80)$$

$$F_D = N_{A0} \frac{dX}{dt} \quad (4-81)$$

Combining Equations (4-79) and (4-81), we have

$$\frac{dV}{dX} = -\alpha N_{A0} \quad (4-82)$$

Integrating yields

$$V = V_0 - \alpha N_{A0} X$$

Rearranging, we have

$$V = V_0(1 + \varepsilon_L X) \quad (4-83)$$

where

$$\varepsilon_L = -\alpha C_{A0} = -\frac{(\text{MW})_D C_{A0}}{\rho}$$

Combining Equation (4-77) for the case of $C_D = 0$ with (4-83), we obtain

$$\frac{dX}{dt} = k C_{A0} \left[\frac{(1 - X)^2}{1 + \varepsilon_L X} \right] \quad (4-84)$$

Using the list of integrals in Appendix A.2, we can determine the true t to achieve a conversion X in the reactor:

$$t = \frac{1}{k C_{A0}} \left[\frac{(1 + \varepsilon_L) X}{1 - X} - \varepsilon_L \ln \frac{1}{1 - X} \right] \quad (4-85)$$

Assuming that product D vaporizes immediately after forming

Second-order reactive distillation

Case 2 Inert gas is bubbled through the reactor

In this case we assume the reaction product is carried off by either "boil off" or an inert gas being bubbled through the reactor. When gas is bubbled through the reactor, we assume vapor-liquid equilibrium and that the mole fractions in the gas and liquid are related by Raoult's law,

$$y_D(g) = x_D(\ell) \frac{P_{vD}}{P_o} = \frac{N_D}{N_A + N_B + N_C + N_D} \frac{P_{vD}}{P_o} \quad (4-86)$$

where P_{vD} is the vapor pressure of D . We now set either the boil off rate by setting the heat flux to the reactor or set the molar flow rate at which an inert is bubbled through the reactor, F_I .

The molar flow rate of D in the gas phase is

$$F_D = y_D F_T$$

Assuming only D evaporates (see the CD-ROM for the situation when this is not the case) the total molar gas flow rate is the inert gas molar flow rate plus the molar flow rate of the evaporating species, in this case species D , is

$$F_T = F_I + F_D = F_I + y_D F_T$$

$$F_T = \frac{F_I}{1 - y_D}$$

The molar flow rate of D leaving the liquid is

$$F_D = \left(\frac{y_D}{1 - y_D} \right) F_I \quad (4-87)$$

This equation is now coupled with all the mole balances, e.g.,

$$\frac{dN_A}{dt} = \frac{-k(N_A N_B - N_C N_D)}{V}$$

$$\vdots$$

$$\frac{dN_D}{dt} = \frac{k(N_A N_B - N_C N_D)}{V} - F_D$$

and solved with an ODE solver.

4.8 Recycle Reactors

Recycle reactors are used when the reaction is autocatalytic, or when it is necessary to maintain nearly isothermal operation of the reactor or to promote a

certain selectivity (see Section 5.6.6). They are also used extensively in biochemical operations. To design recycle reactors, one simply follows the procedure developed in this chapter and then adds a little additional bookkeeping. A schematic diagram of the recycle reactor is shown in Figure 4-15.

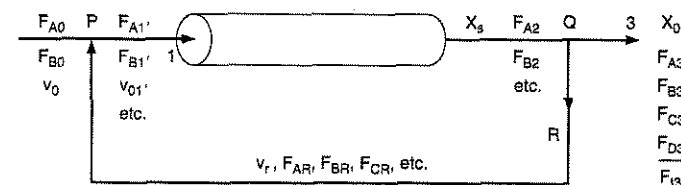


Figure 4-15 Recycle reactor.

The recycled stream is drawn off at point Q and merged with the fresh feed at point P . We shall define the recycle parameter R as the moles recycled per mole of product removed at point Q :

$$R = \frac{F_{IR}}{F_{I3}} = \frac{F_{AR}}{F_{A3}} = \frac{F_{IR}}{F_{I3}}$$

Two conversions are usually associated with recycle reactors: the overall conversion, X_o , and the conversion per pass, X_s :

$$X_s = \frac{\text{moles of A reacted in a single pass}}{\text{mole of A fed to the reactor}} \quad (4-88)$$

$$X_o = \frac{\text{moles of A reacted overall}}{\text{mole of fresh feed}} \quad (4-89)$$

The only new twist in calculating reactor volumes or conversions for a recycle reactor is a mole balance at the stream intersections (points P and Q) to express properly the species concentrations as a function of conversion.

As shown in the CD-ROM, along with the overall conversion and the conversion per pass are related by

$$X_s = \frac{X_o}{1 + R(1 - X_o)} \quad (4-90)$$

The PFR design equation for a recycle reactor is also developed in the CD-ROM.

SUMMARY

1. Solution algorithm

a. Design equations (Batch, CSTR, PBR):

$$N_{A0} \frac{dX}{dt} = -r_A V, \quad V = \frac{F_{A0} X}{-r_A}, \quad F_{A0} \frac{dX}{dW} = -r_A' \quad (S4-1)$$

b. Rate law: for example:

$$-r_A = kC_A^2 \quad (S4-2)$$

c. Stoichiometry:

(1) Gas phase, constant T :

$$v = v_0 \left(\frac{F_T}{F_{T0}} \right) \frac{P_0}{P} = v_0 (1 + \varepsilon X) \frac{P_0}{P} \quad (S4-3)$$

$$C_A = \frac{F_A}{v} = \frac{F_{A0}(1-X)}{v} = \frac{F_{A0}(1-X)}{v_0(1+\varepsilon X)} \left(\frac{P}{P_0} \right) \quad (S4-4)$$

$$= C_{A0} \left(\frac{1-X}{1+\varepsilon X} \right) \left(\frac{P}{P_0} \right)$$

(2) Liquid phase:

$$v = v_0$$

$$C_A = C_{A0}(1-X)$$

d. Combining, we have the following for the gas-phase reaction in a CSTR with no ΔP :

$$V = \frac{F_{A0} X (1 + \varepsilon X)^2}{k C_{A0}^2 (1-X)^2} \quad (S4-5)$$

e. Parameter evaluation:

$$\varepsilon = y_{A0} \delta \quad (S4-6)$$

$$C_{A0} = y_{A0} \left(\frac{P_0}{RT_0} \right) \quad (S4-7)$$

f. Solution techniques:

- (1) Numerical integration—Simpson's rule
- (2) Table of integrals
- (3) Software packages
 - (a) POLYMATH
 - (b) MATLAB

2. Pressure drop in isothermal reactors

a. Variable density with $\varepsilon \neq 0$:

$$y = \frac{P}{P_0}$$

$$\frac{dy}{dW} = \frac{-\alpha}{2y} \left(\frac{F_T}{F_{T0}} \right) \left(\frac{T}{T_0} \right) \quad (S4-8)$$

$$\frac{dy}{dW} = -\frac{\alpha(1+\varepsilon X)}{2y} \left(\frac{T}{T_0} \right) \quad (S4-9)$$

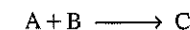
$$\alpha = \frac{2\beta_0}{A_c(1-\phi)\rho_c P_0}$$

$$\beta_0 = \frac{G(1-\phi)}{\rho_0 g_c D_p \phi^3} \left[\frac{150(1-\phi)\mu}{D_p} + 1.75G \right]$$

b. Variable density with $\varepsilon = 0$ or $\varepsilon X \ll 1$ and isothermal:

$$\frac{P}{P_0} = (1 - \alpha W)^{1/2} \quad (S4-10)$$

3. For semibatch reactors, reactant B is fed continuously to a vat initially containing only A:



a. In terms of conversion:

$$N_{A0} \frac{dX}{dt} = -r_A V \quad (S4-11)$$

b. Rate law:

$$-r_A = k \left(C_A C_B - \frac{C_C}{k_C} \right) \quad (S4-12)$$

$$V = V_0 + v_0 t \quad (S4-13)$$

$$C_A = \frac{N_{A0}(1-X)}{V_0 + v_0 t} \quad (S4-14)$$

$$C_B = \frac{N_{B0} + F_{B0}t - N_{A0}X}{V_0 + v_0 t} \quad (S4-15)$$

Equations (S4-11) through (S4-15) are combined and the resulting equation is solved numerically for conversion as a function of time.

c. In terms of concentrations,

$$\frac{dC_A}{dt} = r_A - \frac{C_A v_0}{V} \quad (\text{S4-16})$$

$$\frac{dC_B}{dt} = r_A + \frac{(C_{B0} - C_B)v_0}{V} \quad (\text{S4-17})$$

$$\frac{dC_C}{dt} = -r_A - \frac{C_A v_0}{V} \quad (\text{S4-18})$$

Equations (S4-12), (S4-13), and (S4-16) to (S4-18) are solved simultaneously.

4. Simultaneous reaction and separation

a. Membrane reactors:

$$R_B = k_c C_B \quad (\text{S4-19})$$

b. Reactive distillation:

$$V = V_0(1 + \varepsilon_L X) \quad (\text{S4-20})$$

ODE SOLVER ALGORITHM

When using an ordinary differential equation (ODE) solver such as POLYMATH or MATLAB, it is usually easier to leave the mole balances, rate laws, and concentrations as separate equations rather than combining them into a single equation as we did to obtain an analytical solution. Writing the equations separately leaves it to the computer to combine them and produce a solution. The formulations for a packed-bed reactor with pressure drop and a semibatch reactor are given below for two elementary reactions.

Gas Phase	Liquid Phase
$A + B \rightarrow 3C$	$A + B \rightarrow 2C$
<i>Packed-Bed Reactor</i>	<i>Semibatch Reactor</i>
$\frac{dX}{dW} = \frac{-r_A}{F_{A0}}$	$\frac{dN_A}{dt} = r_A V$
$r_A = -k C_A C_B$	$\frac{dN_B}{dt} = r_A V + F_{B0}$
$C_A = C_{A0} \frac{1-X}{1+\varepsilon X} y$	$\frac{dN_C}{dt} = -2r_A V$
$C_B = C_{A0} \frac{\theta_B - X}{1+\varepsilon X} y$	$V = V_0 + v_0 t$
$\frac{dy}{dW} = -\frac{\alpha(1+\varepsilon X)}{2y}$	$r_A = -k \left[\left(\frac{N_A}{V} \right) \left(\frac{N_B}{V} \right) - \left(\frac{N_C}{V} \right)^2 / K_C \right]$

(where $y = P/P_0$)

$$k = 10.0 \quad K_C = 4.0$$

$$\alpha = 0.01 \quad V_0 = 10.0$$

$$\varepsilon = 0.33 \quad v_0 = 0.1$$

$$\theta_B = 2.0 \quad F_{B0} = 0.02$$

$$C_{A0} = 0.01 \quad N_{A0} = 0.02$$

$$F_{A0} = 15.0 \quad t_{\text{final}} = 200$$

$$W_{\text{final}} = 80$$

QUESTIONS AND PROBLEMS

The subscript to each of the problem numbers indicates the level of difficulty: A, least difficult; D, most difficult.

$$A = \bullet \quad B = \blacksquare \quad C = \blacklozenge \quad D = \blacklozenge\blacklozenge$$

In each of the questions and problems below, rather than just drawing a box around your answer, write a sentence or two describing how you solved the problem, the assumptions you made, the reasonableness of your answer, what you learned, and any other facts that you want to include. You may wish to refer to W. Strunk and E. B. White, *The Elements of Style* (New York: Macmillan, 1979) and Joseph M. Williams, *Style: Ten Lessons in Clarity & Grace* (Glenview, Ill.: Scott, Foresman, 1989) to enhance the quality of your sentences. See the Preface for additional generic parts (x), (y), (z) to the home problems.



P4-1A Read through all the problems at the end of this chapter. Make up and solve an *original* problem based on the material in this chapter. (a) Use real data and reactions. (b) Make up a reaction and data. (c) Use an example from everyday life (e.g., making toast or cooking spaghetti). In preparing your original problem, first list the principles you want to get across and why the problem is important. Ask yourself how your example will be different from those in the text or lecture. Other things for you to consider when choosing a problem are relevance, interest, impact of the solution, time required to obtain a solution, and degree of difficulty. Look through some of the journals for data or to get some ideas for industrially important reactions or for novel applications of reaction engineering principles (the environment, food processing, etc.). The journals listed at the end of Chapter 1 may be useful for part (a). At the end of the problem and solution describe the creative process used to generate the idea for the problem.

P4-2B What if... you were asked to explore the example problems in this chapter to learn the effects of varying the different parameters? This sensitivity analysis can be carried out by either downloading the examples from the WWW or by loading the programs from the CD-ROM supplied with the text. For each of the example problems you investigate, write a paragraph describing your findings.

(a) What if you were asked to give examples of the material in this book that are found in everyday life? What would you say?



- (b) It has come time to replace the catalyst and the supplier inadvertently manufactures and ships you a catalyst whose particle size is one-fourth that of the one you are using. On realizing his mistake, he says that he will sell you the catalyst at his cost, which is roughly half price. Should you accept his offer? Prepare arguments why you should accept the catalyst along with arguments why you should not accept the catalyst.
- (c) After plotting the exit conversion as a function of the pressure drop parameter α in Example 4-7, what generalization can you make? How would your answers change for an equal molar feed? What if the catalyst particles in Example 4-7 were placed in 100 tubes placed in series rather than in 100 tubes placed in parallel?
- (d) Reconsider Example 4-8. Plot the conversion profile for the case when the entering pressure is increased by a factor of 5 and the particle diameter is decreased by a factor of 5. (Recall that α is a function of the particle diameter and P_0 .) What did you learn from your plot? What should be your next settings of α and P_0 to learn more? Assume turbulent flow.
- (e) Consider adding an inert to the reaction in Example 4-9, keeping the total molar flow rate at a constant. Plot the exit conversion and the equilibrium conversion as a function of the mole fraction of an inert. What are the advantages and disadvantages of adding an inert?
- (f) Rework Example 4-10. Plot the molar flow rates of A, B, and C as a function of reactor length (i.e., volume) for different values of k_c between $k_c = 0.0$ (a conventional PFR) and $k_c = 7.0 \text{ min}^{-1}$. What parameters would you expect to affect your results the most? Vary the parameters k, k_c, K_c, F_{A0} to study how the reaction might be optimized. Ask such questions as: What is the effect of the ratio of k to k_c , or of $k_c \tau$ to K_c ? What generalizations can you make? How would your answer change if the reactor temperature were raised significantly? What if someone claimed that membrane reactors were not as safe as semibatch reactors? What would you tell them?
- (g) In Example 4-11, plot the time at which maximum rate of reaction occurs (e.g., in the example the maximum rate is $0.00017 \text{ mol/dm}^3 \cdot \text{s}$ at $t \approx 25 \text{ s}$) as a function of the entering molar feed rate of B. What if you were asked to obtain the maximum concentration of C and D in Example 4-11? What would you do?
- (h) Vary some of the operating costs, conversions, and separations in Figure 4-11 to learn how the profit changes. Ethylene oxide, used to make ethylene glycol, sells for \$0.56/lb. while ethylene glycol sells for \$0.38/lb. Is this a money-losing proposition? Explain.
- (i) What if you assumed that the reaction in Example 4-11 was first-order in methyl amine (B) and zero-order in bromine cyanide. Since it is in excess at the start of the reaction, show that the concentration of methyl amine at any time t is

$$C_B = \left[C_{B0} / \left(1 + \frac{V_0}{v_0} \right) \right] \left[1 - \left(\frac{V_0 + v_0 t}{V_0} \right)^{-1 + k V_0 / v_0} \right]$$

Up to what time and under what conditions is the assumption valid? [See W. Ernst, *AIChE J.*, 43, p. 1114 (1997).]

- (j) What should you do if some of the ethylene glycol splashed out of the reactor onto your face and clothing? (Hint: Recall <http://www.siri.org/>.)



Application
Pending
for Problem
Hall of
Fame

- (k) What safety precautions should you take with the ethylene oxide formation discussed in Example 4-6? With the bromine cyanide discussed in Example 4-11?

P4-3A If it takes 11 minutes to cook spaghetti in Ann Arbor, Michigan, and 14 minutes in Boulder, Colorado, how long would it take in Cuzco, Peru? Discuss ways to make the spaghetti more tasty. If you prefer to make a creative spaghetti dinner for family or friends rather than answering this question, that's OK, too; you'll get full credit. (Ans. $t = 21 \text{ min}$)

P4-4A Nutrition is an important part of ready-to-eat cereal. To make cereal healthier, many nutrients are added. Unfortunately, nutrients degrade over time, making it necessary to add more than the declared amount to assure enough for the life of the cereal. Vitamin X is declared at a level of 20% of the Recommended Daily Allowance per serving size (serving size = 30 g). The Recommended Daily Allowance is 6500 IU ($1.7 \times 10^6 \text{ IU} = 1 \text{ g}$). It has been found that the degradation of this nutrient is first-order in the amount of nutrients. Accelerated storage tests have been conducted on this cereal, with the following results

Temperature ($^{\circ}\text{C}$)	45	55	65
k (week^{-1})	0.0061	0.0097	0.0185

- (a) Given the information above and that the cereal needs to have a vitamin level above the declared value of 6500 IU for 1 year at 25°C , what IU should be present in the cereal at the time it is manufactured? Your answer may also be reported in percent overuse: (Ans. 12%)

$$\% \text{OU} = \frac{C(t=0) - C(t=1 \text{ yr})}{C(t=1 \text{ yr})} \times 100$$

- (b) At what percent of declared value of 6500 IU must you apply the vitamin? If 10,000,000 lb/yr of the cereal is made and the nutrient cost is \$5 per pound, how much will this overuse cost?
- (c) If this were your factory, what percent overuse would you actually apply and why?
- (d) How would your answers change if you stored the material in a Bangkok warehouse for 6 months, where the daily temperature is 40°C , before moving it to the supermarket? (Table of results of accelerated storage tests on cereal; and Problem of vitamin level of cereal after storage courtesy of General Mills, Minneapolis, MN.)

P4-5A The liquid-phase reaction



follows an elementary rate law and is carried out isothermally in a flow system. The concentrations of the A and B feed streams are 2 M before mixing. The volumetric flow rate of each stream is $5 \text{ dm}^3/\text{min}$ and the entering temperature is 300 K. The streams are mixed immediately before entering. Two reactors are available. One is a gray 200.0-dm^3 CSTR that can be heated to 77°C or cooled to 0°C , and the other is a white 800.0-dm^3 PFR operated at 300 K that cannot be heated or cooled but can be painted red or black. Note $k = 0.07 \text{ dm}^3/\text{mol} \cdot \text{min}$ at 300 K and $E = 20 \text{ kcal/mol}$

- (a) Which reactor and what conditions do you recommend? Explain the reason for your choice (e.g., color, cost, space available, weather conditions). Back up your reasoning with the appropriate calculations.

- (b) How long would it take to achieve 90% conversion in a 200-dm³ batch reactor with $C_{A0} = C_{B0} = 1\text{ M}$ after mixing at a temperature of 77°C?
- (c) How would your answer to part (b) change if the reactor were cooled to 0°C? (Ans. 2.5 days)
- (d) What concerns would you have to carry out the reaction at higher temperatures?
- (e) Keeping Table 4-1 in mind, what batch reactor volume would be necessary to process the same amount of species A per day as the flow reactors while achieving not less than 90% conversion? Referring to Table 4-1, estimate the cost of the batch reactor.
- (f) Write a couple of sentences describing what you learned from the problem and what you believe to be the point of the problem.

P4-6_B

Dibutyl phthalate (DBP), a plasticizer, has a potential market of 12 million lb/year (AIChE 1984 Student Contest Problem) and is to be produced by reaction of *n*-butanol with monobutyl phthalate (MBP). The reaction follows an elementary rate law and is catalyzed by H₂SO₄ (Figure P4-6). A stream containing MBP and butanol is to be mixed with the H₂SO₄ catalyst immediately before the stream enters the reactor. The concentration of MBP in the stream entering the reactor is 0.2 lb mol/ft³ and the molar feed rate of butanol is five times that of MBP. The specific reaction rate at 100°F is 1.2 ft³/lb mol·hr. There is a 1000-gallon CSTR and associated peripheral equipment available for use on this project for 30 days a year (operating 24 h/day).

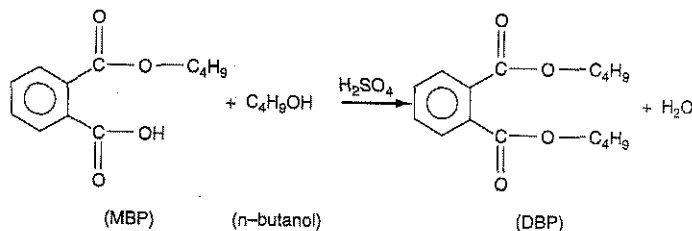
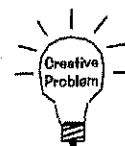


Figure P4-6

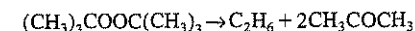
- (a) Determine the exit conversion in the available 1000-gallon reactor if you were to produce 33% of the share (i.e., 4 million lb/yr) of the predicted market. (Ans.: $X = 0.33$).
- (b) How might you increase the conversion and decrease the time of operation? For example, what conversion would be achieved if a second 1000-gal CSTR were placed either in series or in parallel with the CSTR?
- (c) For the same temperature and feed conditions as part (a), what CSTR volume would be necessary to achieve a conversion of 85% for a molar feed rate of A of 1 lb mol/min?
- (d) Compare your results for part (c) with those of the PFR necessary to achieve 85% conversion.
- (e) Keeping in mind the times given in Table 4-1 for filling, and other operations, how many 1000-gallon reactors operated in the batch mode would be necessary to meet the required production of 4 million pounds in a 30-day period? Estimate the cost of the reactors in the system. [Note: Present in the feed stream may be some trace impurities, which you may



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lump as a hexanol. The activation energy is believed to be somewhere around 25 kcal/mol. The PFR in part (d) is more oblong than cylindrical, with a major-to-minor axis ratio of 1.3:1.] (An Ans.: 5 reactors)

P4-7_A The elementary gas-phase reaction

is carried out isothermally in a flow reactor with no pressure drop. The specific reaction rate at 50°C is 10⁻⁴ min⁻¹ (from pericosity data) and the activation energy is 85 kJ/mol. Pure di-*tert*-butyl peroxide enters the reactor at 10 atm and 127°C and a molar flow rate of 2.5 mol/min. Calculate the reactor volume and space time to achieve 90% conversion in:

- (a) a CSTR (Ans.: 4700 dm³)
- (b) a PFR (Ans.: 967 dm³)
- (c) If this reaction is to be carried out at 10 atm and 127°C in a batch mode with 90% conversion, what reactor size and cost would be required to process (2.5 mol/min × 60 min/h × 24 h/day) 3600 mol of di-*tert*-butyl peroxide per day? (Hint: Recall Table 4-1.)
- (d) Assume that the reaction is reversible with $K_C = 0.025\text{ mol}^2/\text{dm}^6$ and calculate the equilibrium conversion and then redo (a) through (c) to achieve a conversion that is 90% of the equilibrium conversion.
- (e) What CSTR temperature would you recommend for a 500-dm³ CSTR to obtain the maximum conversion if $\Delta H_{Rx} = -100,000\text{ cal/mol}$? (Hint: Remember that the equilibrium conversion will be different for a flow reactor and a constant-volume batch reactor for a gas-phase reaction that has a change in the total number of moles.)

P4-8_B A liquid-phase isomerization $A \rightarrow B$ is carried out in a 1000-gal CSTR that has a single impeller located halfway down the reactor. The liquid enters at the top of the reactor and exits at the bottom. The reaction is second-order. Experimental data taken in a batch reactor predicted the CSTR conversion should be 50%. However, the conversion measured in the actual CSTR was 57%.

- (a) Suggest reasons for the discrepancy and suggest something that would give closer agreement between the predicted and measured conversions. Back your suggestions with calculations.
- (b) Consider the case where the reaction is reversible with $K_C = 15$ at 300 K, and $\Delta H_{Rx} = -25,000\text{ cal/mol}$. Assuming that the batch data taken at 300 K are accurate and that $E = 15,000\text{ cal/mol}$, what CSTR temperature do you recommend for maximum conversion?

P4-9 Sargent Nigel Ambercromby. Scoundrels Incorporated, a small R&D company has developed a laboratory scale process for the elementary, solid-catalyzed-gas-phase reaction $A + B \rightarrow C + D$ (names coded for proprietary reasons). The feed is equal molar in A and B with the entering molar flow rate of A is 25 mol/min and the volumetric feed is 50 dm³/min. Engineers at Scoundrels calculated that an industrial scale packed bed reactor with 500 kg of a very rare and expensive metal catalyst will yield a 66% conversion when run at 32°C and a feed pressure of 25 atm. At these conditions the specific reaction rate is 0.4 dm³/mol·min·kg catalyst. Scoundrels sells this process and catalyst to Clueless Chemicals who then manufactured the packed bed. When Clueless put the process onstream at the specifications provided by Scoundrels, they could only achieve 60% conversion with 500 kg catalyst. Unfortunately the reaction was carried out at 31.5°C rather than 32°C. The

corresponding 2160 mol/day of lost product made the process uneconomical. Scoundrels, Inc. say that they can guarantee 66% conversion if Clueless will purchase 500 more kg of catalyst at one and a half times the original cost. As a result, Clueless contacted Sgt. Ambergromby from Scotland Yard (on loan to the L.A.P.D.) about possible industrial fraud. What are the first three questions Sargent Ambergromby asks? What are potential causes for this lost conversion (support with calculations)? What do you think Sgt. Ambergromby suggests to rectify the situation (with Dan Dixon, Reaction Engineering Alumni W'97).

- P4-10_B** The formation of diphenyl discussed in Section 3.1.4 is to be carried out at 760°C. The feed is to be pure benzene in the gas phase at a total pressure of 5 atm and 760°C. The specific reaction rate is 1800 ft³/lb mol · s and the concentration equilibrium constant is 0.3 as estimated by the Davenport trisped oscimeter. The batch reactor volume [part (d)] is 1500 dm³. Also, the inside of the batch reactor is corroding badly, as evidenced by the particulate material that is falling off the sides onto the bottom of the reactor, and you may not need to address this effect.

(a) What is the equilibrium conversion?

Calculate the reactor volume necessary to achieve 98% of the equilibrium conversion of benzene in a

(b) **PFR** (with a benzene feed of 10 lb mol/min)

(c) **CSTR** (with a benzene feed of 10 lb mol/min)

(d) Calculate the volume of a constant-volume batch reactor that processes the same amount of benzene each day as the CSTR. What is the corresponding reactor cost? (Hint: Recall Table 4-1.)

(e) If the activation energy is 30,202 Btu/lb mol, what is the ratio of the initial rate of reaction (i.e., $X = 0$) at 1400°F to that at 800°F?

- P4-11_B** The gaseous reaction $A \longrightarrow B$ has a unimolecular reaction rate constant of 0.0015 min⁻¹ at 80°F. This reaction is to be carried out in parallel tubes 10 ft long and 1 in. inside diameter under a pressure of 132 psig at 260°F. A production rate of 1000 lb/h of B is required. Assuming an activation energy of 25,000 cal/g mol, how many tubes are needed if the conversion of A is to be 90%? Assume perfect gas laws. A and B each have molecular weights of 58. (From California Professional Engineers Exam.)

- P4-12_B** The irreversible elementary reaction $2A \longrightarrow B$ takes place in the gas phase in an isothermal tubular (plug-flow) reactor. Reactant A and a diluent C are fed in equimolar ratio, and conversion of A is 80%. If the molar feed rate of A is cut in half, what is the conversion of A assuming that the feed rate of C is left unchanged? Assume ideal behavior and that the reactor temperature remains unchanged. (From California Professional Engineers Exam.)

- P4-13_B** Compound A undergoes a reversible isomerization reaction, $A \rightleftharpoons B$, over a supported metal catalyst. Under pertinent conditions, A and B are liquid, miscible, and of nearly identical density; the equilibrium constant for the reaction (in concentration units) is 5.8. In a fixed-bed isothermal flow reactor in which backmixing is negligible (i.e., plug flow), a feed of pure A undergoes a net conversion to B of 55%. The reaction is elementary. If a second, identical flow reactor at the same temperature is placed downstream from the first, what overall conversion of A would you expect if:

(a) The reactors are directly connected in series? (Ans.: $X = 0.74$.)

(b) The products from the first reactor are separated by appropriate processing and only the unconverted A is fed to the second reactor?

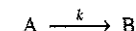
(From California Professional Engineers Exam.)

- P4-14_C** A total of 2500 gal/h of metaxylene is being isomerized to a mixture of orthoxylene, metaxylene, and paraxylene in a reactor containing 1000 ft³ of catalyst. The reaction is being carried out at 750°F and 300 psig. Under these conditions, 37% of the metaxylene fed to the reactor is isomerized. At a flow rate of 1667 gal/h, 50% of the metaxylene is isomerized at the same temperature and pressure. Energy changes are negligible.

It is now proposed that a second plant be built to process 5500 gal/h of metaxylene at the same temperature and pressure as described above. What size reactor (i.e., what volume of catalyst) is required if conversion in the new plant is to be 46% instead of 37%? Justify any assumptions made for the scale-up calculation. (Ans.: 2931 ft³ of catalyst.) (From California Professional Engineers Exam.)

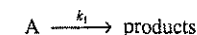
- P4-15_A** It is desired to carry out the gaseous reaction $A \longrightarrow B$ in an existing tubular reactor consisting of 50 parallel tubes 40 ft long with a 0.75-in. inside diameter. Bench-scale experiments have given the reaction rate constant for this first-order reaction as 0.00152 s⁻¹ at 200°F and 0.0740 s⁻¹ at 300°F. At what temperature should the reactor be operated to give a conversion of A of 80% with a feed rate of 500 lb/h of pure A and an operating pressure of 100 psig? A has a molecular weight of 73. Departures from perfect gas behavior may be neglected, and the reverse reaction is insignificant at these conditions. (Ans.: $T = 275^\circ\text{F}$.) (From California Professional Engineers Exam.)

- P4-16_B** An isothermal, constant-pressure plug-flow reactor is designed to give a conversion of 63.2% of A to B for the first-order gas-phase decomposition



for a feed of pure A at a rate of 5 ft³/h. At the chosen operating temperature, the first-order rate constant $k = 5.0 \text{ h}^{-1}$. However, after the reactor is installed and in operation, it is found that conversion is 92.7% of the desired conversion. This discrepancy is thought to be due to a flow disturbance in the reactor that gives rise to a zone of intense backmixing. Assuming that this zone behaves like a perfectly mixed stirred-tank reactor in series and in between two plug-flow reactors, what fraction of the total reactor volume is occupied by this zone? (Ans.: 57%.)

- P4-17_B** Currently, the herbicide atrazine found in the Des Plaines River is being treated by passing part of the river through a marsh, where it is degraded (Figure P4-17). The rate of degradation of atrazine, A, is assumed irreversible and to follow first-order homogeneous kinetics.



As the wastewater flows and reacts, it also evaporates at a constant rate ($Q = \text{kmol water/h} \cdot \text{m}^2$) from the surface. None of the toxic species are lost to the air by evaporation. You may assume that the reactor (marsh) is rectangular and that the gentle downhill flow of the water can be modeled as plug flow.

- (a) Derive an equation for C_A as a function of X and z .
(Ans.: $C_A = C_{A0}(1 - X)/(1 - az)$; $a = QW/\rho_0 v_0$.)
- (b) Derive an equation for X as a function of distance, z , down the wetlands.
(Ans.: $X = 1 - (1 - az)^n$; $n = kD\rho_0/Q$.)
- (c) Plot the conversion and rate of reaction as a function of distance for:
- (1) no evaporation or condensation
 - (2) evaporation but no condensation

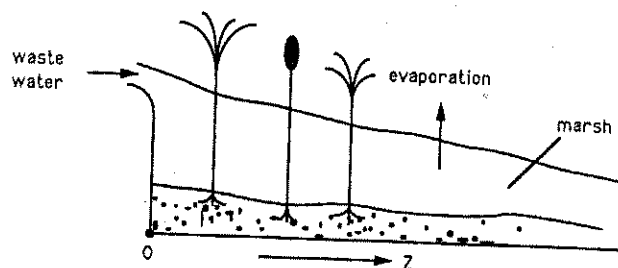


Figure P4-17 [See R. H. Kadlec and R. L. Knight, *Treatment of Wetlands*, CRC Press, Lewis Publishers, Boca Raton, Fla., 1996.]

- (3) condensation at a rate of $0.5 \text{ kmol/m}^2 \cdot \text{h}$. Compare your results for each of the three cases.
- (d) Use POLYMATH to carry out a sensitivity analysis of the various parameter values and their ratios (e.g., what is the effect of this ratio Q/kC_{A0} on the conversion)?
- (e) A heated political battle is currently raging between those who want to preserve wetlands (which are currently protected by law) in their natural state and those who want to make them available for commercial development. List arguments on both sides of this issue, including one or more arising from a consideration of this problem. Then take a position one way or the other and justify it briefly. (Your grade doesn't depend on what position you take, only on how well you defend it.) [Part (e) suggested by Prof. Richard Felder, North Carolina State University.]
- (f) Without solving any equations, suggest a better model for describing the wetlands. (Hint: An extended version of this problem can be found on the CD-ROM.)

Additional information:

W = width = 100 m, v_0 = entering volumetric flow rate = $2 \text{ m}^3/\text{h}$

L = length = 1000 m, C_{A0} = entering concentration of toxic = 10^{-5} mol/dm^3

D = average depth = 0.25 m, ρ_m = molar density of water = $55.5 \text{ kmol H}_2\text{O/m}^3$

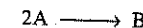
Q = evaporation rate = $1.11 \times 10^{-3} \text{ kmol/h} \cdot \text{m}^2$,

k_1 = specific reaction rate = $16 \times 10^{-5} \text{ h}^{-1}$

- P4-18_B** Ethyl acetate is an extensively used solvent and can be formed by the vapor-phase esterification of acetic acid and ethanol. The reaction was studied using a microporous resin as a catalyst in a packed-bed reactor [Ind. Eng. Chem. Res., 26(2), 198(1987)]. The reaction is first-order in ethanol and pseudo-zero-order in acetic acid. For an equal molar feed rate of acetic acid and ethanol the specific reaction rate is $1.2 \text{ dm}^3/\text{g cat} \cdot \text{min}$. The total molar feed rate is 10 mol/min , the initial pressure is 10 atm, the temperature is 118°C , and the pressure drop parameter, α , equals 0.01 g^{-1} .
- (a) Calculate the maximum weight of catalyst that one could use and maintain an exit pressure above 1 atm. (Ans.: $W = 99 \text{ g}$)
- (b) Determine the catalyst weight necessary to achieve 90% conversion. What is the ratio of catalyst needed to achieve the last 5% (85 to 90%)

conversion to the weight necessary to achieve the first 5% conversion (0 to 5%) in the reactor? Vary α and write a few sentences describing and explaining your findings. (Ans.: $W = 82 \text{ g}$)

P4-19_B The gas-phase dimerization



follows an elementary rate law and takes place isothermally in a PBR charged with 1.0 kg of catalyst. The feed, consisting of pure A, enters the PBR at a pressure of 20 atm. The conversion exiting the PBR is 0.3, and the pressure at the exit of the PBR is 5 atm.

- (a) If the PBR were replaced by a CSTR, what will be the conversion at the exit of the CSTR? You may assume that there is no pressure drop in the CSTR. (Ans.: $X = 0.4$.)
- (b) What would be the conversion in the PBR if the mass flow rate were decreased by a factor of 4 and particle size were doubled? Assume turbulent flow. (Final exam, Winter 1993)
- (c) Discuss the strengths and weaknesses of using this as a final exam problem.

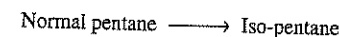
P4-20_D The decomposition of cumene,



is to be carried out at a high temperature in a packed-bed reactor. At this temperature the reaction is internal diffusion limited and apparent first-order in cumene. Currently, 1000 kg of catalyst is packed in a 4-cm diameter pipe. The catalyst particles are 0.5 cm in diameter and the bulk density of the packed catalyst is 1000 kg/m^3 . Currently, 6.4% conversion is realized when pure cumene enters the reactor. The entering pressure is 20 atm and the pressure at the exit of the reactor is 2.46 atm.

- (a) What conversion would be achieved if the PBR were replaced by a fluidized CSTR containing 8000 kg catalyst with negligible pressure drop?
- (b) We know from Chapter 12 [e.g., Equation (12-35)] that for internal diffusion limitations, the rate of reaction varies inversely with the catalyst particle size. Consequently, one of the engineers suggests that the catalyst be ground up into a smaller size. She also notes there are three other pipe sizes available into which the catalyst could be packed. These non-corrosive heat-resistant pipes, which can be cut to any length, are 2 cm, 6 cm, and 8 cm in diameter. Should you change the catalyst size and pipe diameter in which the catalyst is packed? If so, what are the appropriate catalyst particle size, the appropriate pipe diameter, and the exiting conversion? If nothing should be changed, explain your reasoning. Assume that the flow is highly turbulent and that the bulk catalyst density is the same for all catalyst and pipe sizes. Explain how your answers would change if the flow were "laminar."
- (c) Discuss what you learned from this problem and what you believe to be the point of the problem.

P4-21_C The first order irreversible gas phase reaction



is to be carried out in a packed bed reactor. Currently 1000 kg of reforming catalyst are packed in a 4 cm diameter pipe. The catalyst particles are 0.5 cm in diameter and the bulk density of the packed catalyst is $1,000 \text{ kg/m}^3$. Cur-

rently 14.1% conversion is realized. The entering pressure is 20 atm and the pressure at the exit of the reactor is 9.0 atmospheres. It is believed that this reaction is internal diffusion limited. We know from Chapter 12 of Elements of CRE (e.g. P4-23_C or Eqn. 12-35, page 751) that for internal diffusion limitations the rate of reaction varies inversely with the catalyst particle size. Consequently one of the engineers suggests that the catalyst be ground up into a smaller size. She also notes the smallest size to which the catalyst may be ground is 0.01 cm. and that there are 3 other pipe sizes available into which the catalyst could be packed. These non-corrosive heat-resistant pipes, which can be cut to any length, are 2 cm, 3 cm, and 6 cm in diameter.

- (a) What conversion could be achieved in a CSTR with the same catalyst weight and no ΔP ? (Ans.: $X = 0.18$.)
- (b) Calculate the maximum value of the pressure drop parameter, α , that you can have and still maintain an exit pressure of 1 atm. (Ans.: $\alpha = 9.975 \times 10^{-4} \text{ kg}^{-1}$.)
- (c) Should you change the catalyst size and pipe diameter in which 1000 kg of the catalyst is packed while maintaining the catalyst weight?
- (d) Next consider how α would change if you changed both pipe size and particle size. Can you change pipe size and particle size at the same time such that α remains constant at the value calculated in part (b)?
- (e) For the conditions of part (a) [i.e., maintain α constant at the value in part (a)], pick a pipe size and calculate a new particle size. (Ans.: $D_p = 0.044 \text{ cm}$.) Assume turbulent flow.
- (f) Calculate a new specific reaction rate ratio assuming (i.e., recall the effectiveness factor from Chapter 12) that

$$k \sim \frac{1}{D_p} \quad \text{then} \quad k_2 = k_1 \left(\frac{D_{p1}}{D_{p2}} \right)$$

- (g) Using the new values of k and α , calculate the conversion for a PBR for the new particle size for an exit pressure of 1 atm. (Ans.: $X = 0.78$.)

P4-22_B Alkylated cyclohexanols are important intermediates in the fragrance and perfume industry [*Ind. Eng. Chem. Res.*, 28, 693 (1989)]. Recent work has focused on gas-phase catalyzed hydrogenation of *o*-cresol to 2-methylcyclohexanone, which is then hydrogenated to 2-methylcyclohexanol. In this problem we focus on only the first step in the reaction (Figure P4-22). The reaction on a nickel-silica catalyst was found to be zero-order in *o*-cresol and first-order in hydrogen with a specific reaction rate at 170°C of 1.74 mol of *o*-cresol/(kg cat · min · atm). The reaction mixture enters the packed-bed reactor at a total pressure of 5 atm. The molar feed consists of 67% H₂ and 33% *o*-cresol at a total molar rate of 40 mol/min.

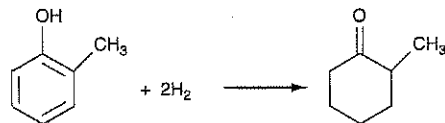


Figure P4-22

- (a) Neglecting pressure drop, plot the rate of reaction of *o*-cresol and the concentrations of each species as a function of catalyst weight. What is the ratio of catalyst weight needed to achieve the last 5% conversion to the weight necessary to achieve the first 5% conversion (0 to 5%) in the plug-flow reactor?
- (b) Accounting for the pressure drop in the packed bed using a value of $\alpha = 0.34 \text{ kg}^{-1}$, redo part (a) along with a plot of pressure versus catalyst weight.
- (c) Another engineer suggests that instead of changing catalyst size it would be better to pack the catalyst in a shorter reactor with twice the pipe diameter. If all other conditions remain the same, is this suggestion better?

P4-23_C The elementary gas-phase reaction



is carried out in a packed-bed reactor. Currently, catalyst particles 1 mm in diameter are packed into 4-in. schedule 40 pipe ($A_c = 0.82126 \text{ dm}^2$). The value of β_0 in the pressure drop equation is 0.001 atm/dm. A stoichiometric mixture of A and B enters the reactor at a total molar flowrate of 10 gmol/min, a temperature of 590 K, and a pressure of 20 atm. Flow is turbulent throughout the bed. Currently, only 12% conversion is achieved with 100 kg of catalyst.

It is suggested that conversion could be increased by changing the catalyst particle diameter. Use the data below to correlate the specific reaction rate as a function of particle diameter. Then use this correlation to determine the catalyst size that gives the highest conversion. As you will see in Chapter 12, k' for first-order reaction is expected to vary according to the following relationship

$$k' = \eta k = \frac{3}{\Phi^2} (\Phi \coth \Phi - 1) k \quad (\text{P4-23.1})$$

where Φ varies directly with particle diameter, $\Phi = c D_p$. Although the reaction is not first-order, one notes from Figure 12-5 the functionality for a second-order reaction is similar to Equation (P4-23.1). (Ans.: $c = 75$)

- (a) Make a plot of conversion as a function of catalyst size.
- (b) Discuss how your answer would change if you had used the effectiveness factor for a second-order reaction rather than a first-order reaction.
- (c) Discuss what you learned from this problem and what you believe to be the point of the problem.

Additional information:

Void fraction = 0.35

Bulk catalyst density = 2.35 kg/dm³

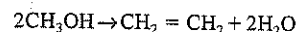
Catalyst Diameter, d_p (mm)	2	1	0.4	0.1	0.02	0.002
k' (dm ⁶ /mol · min · kg cat)	0.06	0.12	0.30	1.2	2.64	3.00

[Hint: You could use Equation (P4.23-1), which would include d_p and an unknown proportionality constant which you could evaluate from the data. For very small values of the Thiele modulus we know $\eta = 1$ and for very large values of the Thiele modulus we know that $\eta = 3/\Phi = 3/CD_p$.]

P4-24_C (Spherical reactor) Because it is readily available from coal, methanol has been investigated as an alternative raw material for producing valuable olefins



such as ethene and propene. One of the first steps in the reforming process involves the dehydration of methanol.



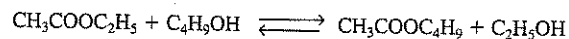
This gas-phase reaction is carried out over a zeolite catalyst and follows an elementary rate law. The catalyst is packed in a tubular PBR that is 2 m in diameter and 22 m in length. Pure methanol is fed at a molar flow rate of 950 mol/s, a pressure of 1500 kPa, a concentration of 0.4 mol/dm³, and 490°C. The conversion and pressure at the exit are 0.5 and 375 kPa, respectively. Flow throughout the bed is known to be such that the turbulent contribution in the Ergun equation (i.e., G^2) can be neglected. The tubular PBR is to be replaced with a spherical PBR containing an equal amount of identical catalyst. The spherical PBR measures 5.2 m in diameter and has screens placed 2 dm from each end (i.e., $L = L' = 24$ dm).

- What conversion and exit pressure can we expect from the spherical reactor? [Hint: What are the parameter values (e.g., α , k) for the PBR ($0.1 < k < 1.0$)? (Ans.: $X = 0.63$.)]
- By how much can the feed rate to the spherical PBR be increased and still achieve the same conversion that was attained in the tubular PBR? Assume that the flow is completely laminar up to $F_{A0} = 2000$ mol/s.
- It is desired to minimize the pumping requirement for the feed to the spherical PBR. How low can the entry pressure, P_0 , be and still achieve a conversion of 0.5?
- Put two spherical PBRs in series. What is the conversion and pressure at the exit? Experiment with putting more than two reactors in series. What is the maximum attainable conversion?

[The data given in this problem are based on kinetics data given in H. Schoenfelder, J. Hinderer, J. Werther, F.J. Keil, Methanol to olefins—prediction of the performance of a circulating fluidized-bed reactor on the basis of kinetic experiments in a fixed-bed reactor. *Chem. Eng. Sci.* 49, 5377 (1994).]

- 4-25_A A very proprietary industrial waste reaction which we'll code as $A \rightarrow B + S$ to be carried out in a 10-dm³ CSTR followed by 10-dm³ PFR. The reaction is elementary, but A, which enters at a concentration of 0.001 mol/dm³ and a molar flow rate of 20 mol/min, has trouble decomposing. The specific reaction rate at 42°C (i.e., room temperature in the Mojave desert) is 0.0001 s⁻¹. However, we don't know the activation energy; therefore, we cannot carry out this reaction in the winter in Michigan. Consequently this reaction, while important, is not worth your time to study. Therefore, perhaps you want to take a break and go watch a movie such as *Dances with Wolves* (a favorite of the author) or *Evita* or the *Sixth Sense*.

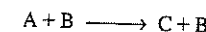
- P4-26_B Pure butanol is to be fed into a *semibatch reactor* containing pure ethyl acetate to produce butyl acetate and ethanol. The reaction



is elementary and reversible. The reaction is carried out isothermally at 300 K. At this temperature the equilibrium constant is 1.08 and the specific reaction rate is 9×10^{-5} dm³/mol·s. Initially, there is 200 dm³ of ethyl acetate in the vat and butanol is fed at a rate of 0.05 dm³/s. The feed and initial concentrations of butanol and ethyl acetate are 10.93 mol/dm³ and 7.72 mol/dm³, respectively.

- Plot the equilibrium conversion of ethyl acetate as a function of time.
- Plot the conversion of ethyl acetate, the rate of reaction, and the concentration of butanol as a function of time.
- Repeat parts (a) and (b) for different values of the butanol feed rate and of the amount of ethyl acetate in the vat.
- Rework part (b) assuming that ethanol evaporates (reactive distillation) as soon as it forms.
- Use POLYMATH or some other ODE solver to learn the sensitivity of conversion to various combinations of parameters.
- Discuss what you learned from this problem and what you believe to be the point of this problem.

- P4-27_B A catalyst is a material that affects the rate of a chemical reaction, yet emerges unchanged from the reaction. For example, consider the reaction



in which

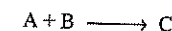
$$r_A = -kC_A C_B$$

where B is a catalyst. The reaction is taking place in a *semibatch reactor*, in which 100 ft³ of a solution containing 2 lb mol/ft³ of A is initially present. No B is present initially. Starting at time $t = 0$, 5 ft³/min of a solution containing 0.5 lb mol/ft³ of B is fed into the reactor. The reactor is isothermal, and $k = 0.2$ ft³/lb mol·min.

- How many moles of C are present in the reactor after half an hour?
- Plot the conversion as a function of time.
- Repeat parts (a) and (b) for the case when the reactor initially contains 100 ft³ of B and A is fed to the reactor at a concentration of 0.02 lb mol/ft³ and at a rate of 5 ft³/min. The feed concentration of B is 0.5 lb mol/ft³.
- Discuss what you learned from this problem and what you believe to be the point of this problem.

- P4-28_C An isothermal reversible reaction $A \rightleftharpoons B$ is carried out in an aqueous solution. The reaction is first-order in both directions. The forward rate constant is 0.4 h⁻¹ and the equilibrium constant is 4.0. The feed to the plant contains 100 kg/m³ of A and enters at the rate of 12 m³/h. Reactor effluents pass to a separator, where B is completely recovered. The reactor is a *stirred tank* of volume 60 m³. A fraction of the unreacted effluent is recycled as a solution containing 100 kg/m³ of A and the remainder is discarded. Product B is worth \$2 per kilogram and operating costs are \$50 per cubic meter of solution entering the separator. What value of f maximizes the operational profit of the plant? What fraction A fed to the plant is converted at the optimum? (H. S. Shankar, IIT Bombay)

- P4-29_B (CSTR train) The elementary liquid-phase reaction



is to be carried out in a CSTR with three impellers (Figure P4-29). The mixing patterns in the CSTR are such that it is modeled as three equal-sized CSTRs in series. Species A and B are fed in separate lines to the CSTR, which is initially filled with inert material. Each CSTR is 200 dm³ and the volumetric flow to the first reactor is 10 dm³/min of A and 10 dm³/min of B.

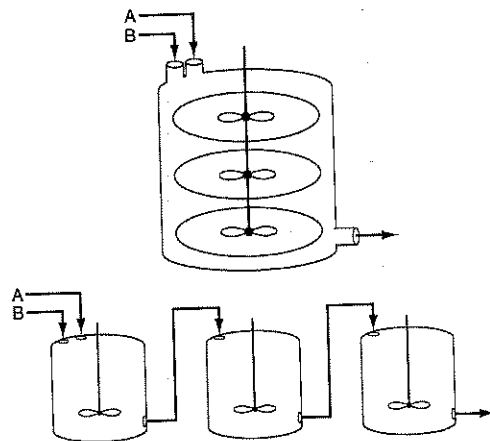


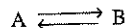
Figure P4-29

- What is the steady-state conversion of A? (Ans.: $X \approx 0.55$)
- Determine the time necessary to reach steady state (i.e., when C_A exiting the third reactor is 99% of the steady-state value).
- Plot the concentration of A exiting each tank as a function of time.
- Suppose that the feed for species B is split so that half is fed to the first tank and half to the second tank. Repeat parts (a), (b), and (c).
- Vary the system parameters, v_0 , V , k , and so on, to determine their effects on startup. Write a paragraph describing the trends you found which includes a discussion of the parameter that most effects the results.

Additional information:

$$C_{A0} = C_{B0} = 2.0 \text{ mol/dm}^3 \quad k = 0.025 \text{ dm}^3/\text{mol} \cdot \text{min}$$

P4-30_B The reversible isomerization



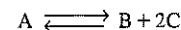
is to be carried out in a *membrane reactor* (IMRCF). Owing to the configuration of species B, it is able to diffuse out the walls of the membrane, while A cannot.

- What is the equilibrium conversion assuming that B does not diffuse out of the reactor walls?
- Plot the conversion profiles to compare a 100-dm³ conventional PFR with a 100-dm³ membrane reactor. What statements or generalizations can you make? What parameters have the greatest effect on the exit conversion shape of the plots in part (a)?
- Plot the conversion and the species concentrations and the molar flow rates down the length of the reactor.
- Vary some of the parameters (e.g., $k = 0.8 \text{ s}^{-1}$, $k_c = 0.03 \text{ s}^{-1}$, $K_c = 1.0$, etc.) and write a paragraph describing your results.
- Discuss how your curves would change if the temperature were increased significantly or decreased significantly for an exothermic reaction and for an endothermic reaction.

Additional information:

$$\begin{aligned} \text{Specific reaction rate} &= 0.05 \text{ s}^{-1} \\ \text{Transport coefficient } k_c &= 0.3 \text{ s}^{-1} \\ \text{Equilibrium constant } K_c &= 0.5 \\ \text{Entering volumetric flow rate } v_0 &= 10 \text{ dm}^3/\text{s} \\ C_{A0} &= 0.2 \text{ mol/dm}^3 \end{aligned}$$

P4-31_C (Membrane reactor) The first-order, reversible reaction



is taking place in a membrane reactor. Pure A enters the reactor, and B diffuses through the membrane. Unfortunately, some of the reactant A also diffuses through the membrane.

- Plot the flow rates of A, B, and C down the reactor, as well as the flow rates of A and B through the membrane.
- Compare the conversion profiles of a conventional PFR with those of an IMRCF. What generalizations can you make?
- Discuss how your curves would change if the temperature were increased significantly or decreased significantly for an exothermic reaction and for an endothermic reaction.

Additional information:

$$\begin{aligned} k &= 10 \text{ min}^{-1} & F_{A0} &= 100 \text{ mol/min} \\ K_c &= 0.01 \text{ mol}^2/\text{dm}^6 & v_0 &= 100 \text{ dm}^3/\text{min} \\ k_{CA} &= 1 \text{ min}^{-1} & V_{\text{reactor}} &= 20 \text{ dm}^3 \\ k_{CB} &= 40 \text{ min}^{-1} \end{aligned}$$

NOTE TO INSTRUCTORS: Additional problems (cf. those from the preceding edition) can be found in the solutions manual and on the CD-ROM. These problems could be photocopied and used to help reinforce the fundamental principles discussed in this chapter.

JOURNAL CRITIQUE PROBLEMS

- P4C-1** In the article describing the liquid reaction of isoprene and maleic anhydride under pressure [*AIChE J.*, 16(5), 766 (1970)], the authors show the reaction rate to be greatly accelerated by the application of pressure. For an equimolar feed they write the second-order reaction rate expression in terms of the mole fraction y :

$$\frac{dy}{dt} = -k_y y^2$$

and then show the effect of pressure on k_y (s^{-1}). Derive this expression from first principles and suggest a possible logical explanation for the increase in the true specific reaction rate constant k ($\text{dm}^3/\text{mol} \cdot \text{s}$) with pressure that is different from the authors'. Make a quick check to verify your challenge.

- P4C-2** The reduction of NO by char was carried out in a fixed bed between 500 and 845°C [*Int. Chem. Eng.*, 20(2), 239, (1980)]. It was concluded that the reaction is first-order with respect to the concentration of NO feed (300 to 1000 ppm) over the temperature range studied. It was also found that activation energy begins to increase at about 680°C. Is first-order the true reaction

order? If there were discrepancies in this article, what might be the reasons for them?

- P4C-3** In the article describing vapor phase esterification of acetic acid with ethanol to form ethyl acetate and water [*Ind. Eng. Chem. Res.*, 26(2), 198 (1987)], the pressure drop in the reactor was accounted for in a most unusual manner [i.e., $P = P_0(1 - fX)$, where f is a constant].
- Using the Ergun equation along with estimating some of the parameter values (e.g., $\phi = 0.4$), calculate the value of α in the packed-bed reactor (2 cm ID by 67 cm long).
 - Using the value of α , redo part (a) accounting for pressure drop along the lines described in this chapter.
 - Finally, if possible, estimate the value of f used in these equations.

SOME THOUGHTS ON CRITIQUING WHAT YOU READ

Your textbooks after your graduation will be, in part, the professional journals that you read. As you read the journals, it is important that you study them with a critical eye. You need to learn if the author's conclusion is supported by the data, if the article is new or novel, if it advances our understanding, and to learn if the analysis is current. To develop this technique, one of the major assignments used in the graduate course in chemical reaction engineering at the University of Michigan for the past 20 years has been an in-depth analysis and critique of a journal article related to the course material. Significant effort is made to ensure that a cursory or superficial review is not carried out. Students are asked to analyze and critique ideas rather than ask questions such as: Was the pressure measured accurately? They have been told that they are not required to find an error or inconsistency in the article to receive a good grade, but if they do find such things, it just makes the assignment that much more enjoyable. Beginning with Chapter 4, a number of the problems at the end of each chapter in this book are based on students' analyses and critiques of journal articles and are designated with a C (e.g., P4C-1). These problems involve the analysis of journal articles that may have minor or major inconsistencies. A discussion on critiquing journal articles can be found on the CD-ROM.

CD-ROM MATERIAL

• Learning Resources

- Summary Notes for Lectures 4, 5, 6, 7, 8 and 9
- Web Modules
 - Wetlands
 - Membrane Reactors
 - Reactive Distillation
- Interactive Computer Modules
 - Mystery Theater
 - Tic-Tac
- Solved Problems
 - CDP4-A_B A Sinister Gentleman Messing with a Batch Reactor

B. Solution to California Registration Exam Problem

C. Ten Types of Home Problems: 20 Solved Problems

- Analogy of CRE Algorithms to a Menu in a Fine French Restaurant
- Algorithm for Gas Phase Reaction

• Living Example Problems

- Example 4-7 Pressure Drop with Reaction-Numerical Solution
- Example 4-8 Dehydrogenation in a Spherical Reactor
- Example 4-9 Working in Terms of Molar Flow Rate in a PFR
- Example 4-10 Membrane Reactor
- Example 4-11 Isothermal Semibatch Reactor with a Second-order Reaction

• Professional Reference Shelf

- Time to Reach Steady State for a 1st Order Reaction in a CSTR
- Recycle Reactors
- Critiquing Journal Articles

- FAQ [Frequently Asked Questions]— In Updates/FAQ icon section
- Additional Homework Problems

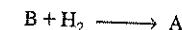
CDP4-A_B A sinister gentlemen is interested in producing methyl perchlorate in a batch reactor. The reactor has a strange and unsettling rate law. [2nd Ed. P4-28]

CDP4-B_C (*Ecological Engineering*) A much more complicated version of Problem 4-17 uses actual pond (CSTR) sizes and flow rates in modeling the site with CSTRs for the Des Plaines River experimental wetlands site (EW3) in order to degrade atrazine.

CDP4-C_B The rate of binding ligands to receptors is studied in this application of reaction kinetics to *bioengineering*. The time to bind 50% of the ligands to the receptors is required. [2nd Ed. P4-34]

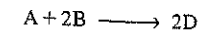
CDP4-D_B A batch reactor is used for the bromination of p-chlorophenyl isopropyl ether; calculate the batch reaction time. [2nd Ed. P4-29]

CDP4-E_B California Professional Engineers Exam Problem in which the reaction



is carried out in a batch reactor. [2nd Ed. P4-15]

CDP4-F_A The gas-phase reaction

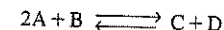


has the rate law $-r_A = 2.5C_A^{1/2}C_B$. Reactor volumes of PFRs and CSTRs are required in this multipart problem. [2nd Ed. P4-21]

CDP4-G_B What type and arrangement of flow reactors should you use for a decomposition reaction with the rate law $-r_A = k_1C_A^{1/2}/(1 + k_2C_A)$? [2nd Ed. P4-14]

CDP4-H_A Verify that the liquid-phase reaction of 5, 6-benzoquinoline with hydrogen is pseudo-first-order. [2nd Ed. P4-7]

CDP4-I_B The liquid-phase reaction



is carried out in a semibatch reactor. Plot the conversion, volume, and species concentration as a function of time. Reactive distillation is also considered in part (e). [2nd Ed. P4-27]

CDP4-J_B Designed to reinforce the basic CRE principles through very straight forward calculations of CSTR and PFR volumes and a batch reactor

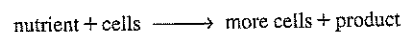
- time. This problem was one of the most often assigned problems from the 2nd Edition. [2nd Ed. P4-4]
- CDP4-K_B** Calculate the overall conversion for *PFR with recycle*. [2nd Ed. P4-28]
- CDP4-L_B** The overall conversion is required in a *packed-bed reactor with recycle*. [2nd Ed. P4-22]
- CDP4-M_B** A recycle reactor is used for the reaction



- in which species C is partially condensed. The PFR reactor volume is required for 50% conversion. [2nd Ed. P4-32]
- CDP4-N_B** Radial flow reactors can be used to good advantage for exothermic reactions with large heats of reaction. The radial velocity varies as

$$U = \frac{U_0 R_0}{r} (1 + \varepsilon X) \frac{P_0}{P} \frac{T}{T_0}$$

- Vary the parameters and plot X as a function of r. [2nd Ed. P4-31]
- CDP4-O_B** The growth of a bacterium is to be carried out in excess nutrient.



The growth rate law is

$$r_B = \mu_m C_B \left(1 - \frac{C_B}{C_{B\max}} \right)$$

- CDP4-P_B** A not very good semibatch problem, but it does require assessing what equation to use.

SUPPLEMENTARY READING

- HILL, C. G., *An Introduction to Chemical Engineering Kinetics and Reactor Design*. New York: Wiley, 1977, Chap. 8.
- LEVENSPIEL, O., *Chemical Reaction Engineering*, 2nd ed. New York: Wiley, 1972, Chaps. 4 and 5.
- SMITH, J. M., *Chemical Engineering Kinetics*, 3rd ed. New York: McGraw-Hill, 1981.
- STEPHENS, B., *Chemical Kinetics*, 2nd ed. London: Chapman & Hall, 1970, Chaps. 2 and 3.
- ULRICH, G. D., *A Guide to Chemical Engineering Reactor Design and Kinetics*. Printed and bound by Braun-Brumfield, Inc., Ann Arbor, Mich., 1993.
- WALAS, S. M., *Reaction Kinetics for Chemical Engineers*. New York: McGraw-Hill, 1970.

Recent information on reactor design can usually be found in the following journals: *Chemical Engineering Science*, *Chemical Engineering Communications*, *Industrial and Engineering Chemistry Research*, *Canadian Journal of Chemical Engineering*, *AIChE Journal*, *Chemical Engineering Progress*.

Collection and Analysis of Rate Data 5

You can observe a lot just by watching.

Yogi Berra, New York Yankees

In Chapter 4 we showed that once the rate law is known, it can be substituted into the appropriate design equation, and through the use of the appropriate stoichiometric relationships we can size any isothermal reaction system. In this chapter we focus on ways of obtaining and analyzing reaction rate data to obtain the rate law for a specific reaction. In particular, we discuss two common types of reactors for obtaining rate data: the batch reactor, which is used primarily for homogeneous reactions, and the differential reactor, which is used for solid-fluid reactions. In batch reactor experiments, concentration, pressure, and/or volume are usually measured and recorded at different times during the course of the reaction. Data are collected from the batch reactor during unsteady-state operation, whereas measurements on the differential reactor are made during steady-state operation. In experiments with a differential reactor, the product concentration is usually monitored for different feed conditions.

Two techniques of data acquisition are presented: concentration-time measurements in a batch reactor and concentration measurements in a differential reactor. Six different methods of analyzing the data collected are used: the differential method, the integral method, the method of half-lives, method of initial rates, and linear and nonlinear regression (least-squares analysis). The differential and integral methods are used primarily in analyzing batch reactor data. Because a number of software packages (e.g., POLYMATH, MATLAB) are now available to analyze data, a rather extensive discussion of linear and nonlinear regression is included. We close the chapter with a discussion of experimental planning and of laboratory reactors (CD-ROM).

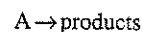
5.1 Batch Reactor Data

Batch reactors are used primarily to determine rate law parameters for homogeneous reactions. This determination is usually achieved by measuring concentration as a function of time and then using either the differential, integral, or least squares method of data analysis to determine the reaction order, α , and specific reaction rate, k . If some reaction parameter other than concentration is monitored, such as pressure, the mole balance must be rewritten in terms of the measured variable (e.g., pressure).

Process data in terms of the measured variable

5.1.1 Differential Method of Rate Analysis

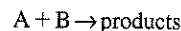
When a reaction is *irreversible*, it is possible in many cases to determine the reaction order α and the specific rate constant by numerically differentiating *concentration versus time data*. This method is applicable when reaction conditions are such that the rate is essentially a function of the concentration of only one reactant: for example, if, for the decomposition reaction



$$-r_A = kC_A^\alpha \quad (5-1)$$

then the differential method may be used.

However, by utilizing the method of excess, it is also possible to determine the relationship between $-r_A$ and the concentration of other reactants. That is, for the irreversible reaction



with the rate law

$$-r_A = k_A C_A^\alpha C_B^\beta \quad (5-2)$$

where α and β are both unknown, the reaction could first be run in an excess of B so that C_B remains essentially unchanged during the course of the reaction and

$$-r_A = k' C_A^\alpha \quad (5-3)$$

where

$$k' = kC_B^\beta \approx kC_{B0}^\beta \quad (5-4)$$

After determining α , the reaction is carried out in an excess of A, for which the rate law is approximated as

$$-r_A = k'' C_B^\beta \quad (5-5)$$

Once α and β are determined, k_A can be calculated from the measurement of $-r_A$ at known concentrations of A and B:

Assume that the rate law is of the form $-r_A = kC_A^\alpha$

Constant-volume batch reactor

$$k_A = \frac{-r_A}{C_A^\alpha C_B^\beta} = (\text{dm}^3/\text{mol})^{\alpha+\beta-1}/\text{s}$$

Both α and β can be determined by using the method of excess, coupled with a differential analysis of data for batch systems.

To outline the procedure used in the differential method of analysis, we consider a reaction carried out isothermally in a constant-volume batch reactor and the concentration recorded as a function of time. By combining the mole balance with the rate law given by Equation (5-1), we obtain

$$-\frac{dC_A}{dt} = k_A C_A^\alpha \quad (5-6)$$

After taking the natural logarithm of both sides of Equation (5-6),

$$\ln \left(-\frac{dC_A}{dt} \right) = \ln k_A + \alpha \ln C_A \quad (5-7)$$

observe that the slope of a plot of $\ln(-dC_A/dt)$ as a function of $(\ln C_A)$ is the reaction order (Figure 5-1).

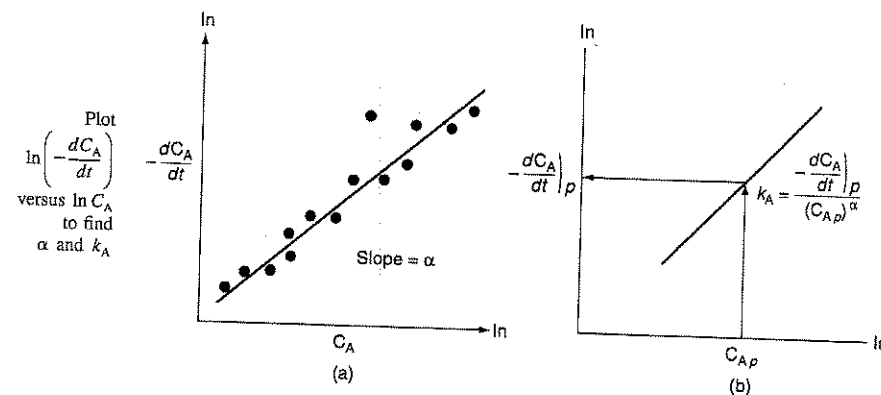


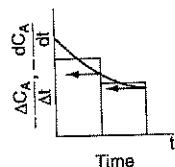
Figure 5-1 Differential method to determine reaction order.

Figure 5-1(a) shows a plot of $-(dC_A/dt)$ versus C_A on log-log paper where the slope is equal to the reaction order α . The specific reaction rate, k_A , can be found by first choosing a concentration in the plot, say C_{Ap} , and then finding the corresponding value of $-(dC_A/dt)$ as shown in Figure 5-1(b). After raising C_{Ap} to the α power, we divide it into $-(dC_A/dt)_p$ to determine k_A :

$$k_A = \frac{-(dC_A/dt)_p}{(C_{Ap})^\alpha}$$

To obtain the derivative $-dC_A/dt$ used in this plot, we must differentiate the concentration-time data either numerically or graphically. We describe three methods to determine the derivative from data giving the concentration as a function of time. These methods are:

- Graphical differentiation
- Numerical differentiation formulas
- Differentiation of a polynomial fit to the data



See Appendix A.2.

Graphical Method. With this method disparities in the data are easily seen. As explained in Appendix A.2, the graphical method involves plotting $\Delta C_A/\Delta t$ as a function of t and then using equal-area differentiation to obtain dC_A/dt . An illustrative example is also given in Appendix A.2.

In addition to the graphical technique used to differentiate the data, two other methods are commonly used: differentiation formulas and polynomial fitting.

Numerical Method. Numerical differentiation formulas can be used when the data points in the independent variable are *equally spaced*, such as $t_1 - t_0 = t_2 - t_1 = \Delta t$:

Time (min)	t_0	t_1	t_2	t_3	t_4	t_5
Concentration (mol/dm ³)	C_{A0}	C_{A1}	C_{A2}	C_{A3}	C_{A4}	C_{A5}

The three-point differentiation formulas¹

$$\text{Initial point: } \left(\frac{dC_A}{dt}\right)_{t_0} = \frac{-3C_{A0} + 4C_{A1} - C_{A2}}{2\Delta t} \quad (5-8)$$

$$\text{Interior points: } \left(\frac{dC_A}{dt}\right)_{t_i} = \frac{1}{2\Delta t} [(C_{A(i+1)} - C_{A(i-1)})] \quad (5-9)$$

$$\left[\text{e.g., } \left(\frac{dC_A}{dt}\right)_{t_3} = \frac{1}{2\Delta t} [C_{A4} - C_{A2}] \right]$$

$$\text{Last point: } \left(\frac{dC_A}{dt}\right)_{t_5} = \frac{1}{2\Delta t} [C_{A3} - 4C_{A4} + 3C_{A5}] \quad (5-10)$$

Methods for finding $-dC_A/dt$ from concentration-time data

can be used to calculate dC_A/dt . Equations (5-8) and (5-10) are used for the first and last data points, respectively, while Equation (5-9) is used for all intermediate data points.

¹ B. Carnahan, H. A. Luther, and J. O. Wilkes, *Applied Numerical Methods* (New York: Wiley, 1969), p. 129.

Polynomial Fit. Another technique to differentiate the data is to first fit the concentration-time data to an n th-order polynomial:

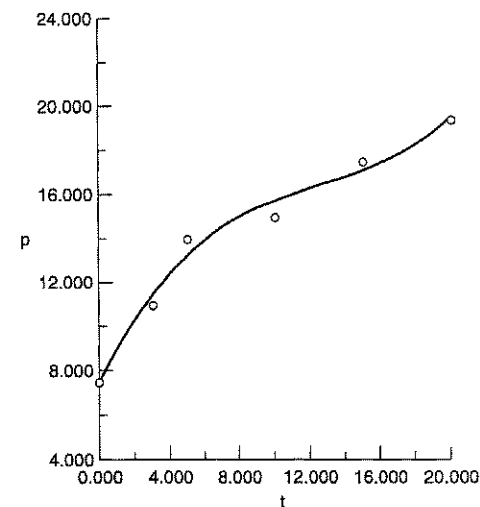
$$C_A = a_0 + a_1t + a_2t^2 + \dots + a_nt^n \quad (5-11)$$

Many personal computer software packages contain programs that will calculate the best values for the constants a_i . One has only to enter the concentration-time data and choose the order of the polynomial. After determining the constants, a_i , one has only to differentiate Equation (5-11) with respect to time:

$$\frac{dC_A}{dt} = a_1 + 2a_2t + 3a_3t^2 + \dots + na_nt^{n-1} \quad (5-12)$$

Thus concentration and the time rate of change of concentration are both known at any time t .

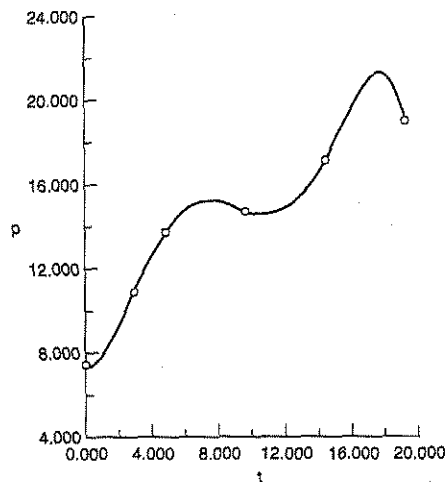
Care must be taken in choosing the order of the polynomial. If the order is too low, the polynomial fit will not capture the trends in the data and not go through many of the points. If too large an order is chosen, the fitted curve can have peaks and valleys as it goes through most all of the data points, thereby producing significant errors when the derivatives, dC_A/dt , are generated at the various points. An example of this is shown in Figure 5-2, where the same pressure-time data fit to a third-order polynomial (a) and to a fifth-order polynomial (b). Observe how the derivative for the fifth order changes from a positive value at 15 minutes to a negative value at 20 minutes.



$$p(t) = 7.50167 + 1.59822t - 0.105874t^2 + 0.00279741t^3$$

(a) variance = 0.738814

Figure 5-2 Polynomial fit of concentration-time data.



$$(b) \quad p(t) = 7.5 - 0.305644t + 0.86538t^2 - 0.151976t^3 + 0.00965104t^4 - 0.000205154t^5$$

Figure 5-2 (continued)

Finding α and k . Now, using either the graphical method, differentiation formulas or the polynomial derivative, the following table can be set up:

Time	t_0	t_1	t_2	t_3
Concentration	C_{A0}	C_{A1}	C_{A2}	C_{A3}
Derivative	$\left(-\frac{dC_A}{dt}\right)_0$	$\left(-\frac{dC_A}{dt}\right)_1$	$\left(-\frac{dC_A}{dt}\right)_2$	$\left(-\frac{dC_A}{dt}\right)_3$

The reaction order can now be found from a plot of $\ln(-dC_A/dt)$ as a function of $\ln C_A$, as shown in Figure 5-1(a), since

$$\ln\left(-\frac{dC_A}{dt}\right) = \ln k_A + \alpha \ln C_A \quad (5-7)$$

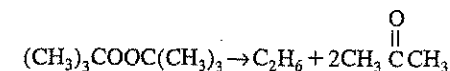
Before solving an example problem let's list the steps to determine the reaction rate law from a set of data points (Table 5-1).

TABLE 5-1. STEPS IN ANALYZING RATE DATA

1. Postulate a rate law.
2. Process your data in terms of the measured variable (rewrite the mole balance in terms of the measured variable).
3. Look for simplifications.
4. Calculate $-r_A$ as a function of reactant concentration to determine the reaction order.
 - a. If batch:
Determine $-dC_A/dt$.
 - b. If differential packed-bed reactor (Section 5.3):
Calculate $-r'_A = F_{A0}X/W = C_P v_0/W$.
5. Determine specific reaction rate, k .

Example 5-1 Differential Method of Analysis of Pressure-Time Data

Determine the reaction order for the gas-phase decomposition of di-*tert*-butyl peroxide,



This reaction was carried out in the laboratory in an isothermal batch system in which the total pressure was recorded at various times during the reaction.² The data given in Table E5-1.1 apply to this reaction. Only pure di-*tert*-butyl peroxide was initially present in the reaction vessel.

TABLE E5-1.1 PRESSURE-TIME DATA

Time (min)	Total Pressure (mmHg)
0.0	7.5
2.5	10.5
5.0	12.5
10.0	15.8
15.0	17.9
20.0	19.4

While the proper SI units of pressure are pascal (Pa) or kilopascal (kPa), a significant amount of kinetic data in past literature are reported in units of mmHg (torr), atmospheres, or psi. Consequently, we must be able to analyze pressure-time rate data in any one of these units.

$$1 \text{ atm} = 14.7 \text{ psi} = 1.103 \text{ bar} = 101.3 \text{ kPa} = 760 \text{ mmHg}$$

Solution

Let A represent di-*tert*-butyl peroxide.

1. Postulate a rate law.

$$-r_A = kC_A^\alpha$$

A combination of the *mole balance* on a constant-volume batch reactor and the *rate law* gives

$$\frac{-dC_A}{dt} = -r_A = kC_A^\alpha \quad (\text{E5-1.1})$$

where α and k are to be determined from the data listed in Table E5-1.1.

Need
 $C_A = f(P)$

² A. F. Trotman-Dickenson, *J. Chem. Educ.*, 46, 396 (1969).

Processing data
in terms of the
measured
variable, P

2. Rewrite the design equation in terms of the measured variable. When there is a net increase or decrease in the total number of moles in a gas phase reaction, the reaction order may be determined from experiments performed with a constant-volume batch reactor by monitoring the total pressure as a function of time. The total pressure data **should not be converted** to conversion and then analyzed as conversion-time data just because the design equations are written in terms of the variable conversions. Rather, **transform the design equation to the measured variable**, which in this case is pressure. Consequently, we need to *express the concentration in terms of total pressure* and then substitute for the concentration of A in Equation (E5-1.1).

For the case of a constant-volume batch reactor, we recall Equations (3-26) and (3-38):

$$C_A = C_{A0}(1 - X) \quad (3-26)$$

$$V = V_0 \frac{P_0}{P} (1 + \epsilon X) \frac{T}{T_0} \quad (3-38)$$

For isothermal operation and constant volume, Equation (3-38) solves to

$$X = \frac{1}{\epsilon P_0} (P - P_0) = \frac{1}{\gamma_{A0} \delta P_0} (P - P_0)$$

$$X = \frac{1}{\delta P_{A0}} (P - P_0) \quad (E5-1.2)$$

where

$$P_{A0} = \gamma_{A0} P_0$$

Combining Equations (3-26) and (E5-1.2) gives

$$C_A = \frac{P_{A0} - [(P - P_0)/\delta]}{RT} \quad (E5-1.3)$$

For pure di-*tert*-butyl peroxide, initially $\gamma_{A0} = 1.0$ and therefore $P_{A0} = P_0$. Stoichiometry gives $\delta = 1 + 2 - 1 = 2$.

$$C_A = \frac{P_0 - [(P - P_0)/2]}{RT} = \frac{3P_0 - P}{2RT} \quad (E5-1.4)$$

Substitute Equation (E5-1.4) into (E5-1.1) to get

$$\frac{1}{2RT} \frac{dP}{dt} = k \left(\frac{3P_0 - P}{2RT} \right)^\alpha$$

Let $k' = k(2RT)^{1-\alpha}$; then

$$\frac{dP}{dt} = k'(3P_0 - P)^\alpha \quad (E5-1.5)$$

Mole balance
in terms of the
measured
variable, P

First find $\frac{dP}{dt}$

Graphical method is
used to visualize
discrepancies in data

Taking the natural logarithm of both sides gives us

$$\ln \frac{dP}{dt} = \alpha \ln(3P_0 - P) + \ln k' \quad (E5-1.6)$$

Observe that the reaction order, α , can be determined from the slope of a plot of $\ln(dP/dt)$ versus $\ln(3P_0 - P)$. Once α is known, the constant k' may be calculated from the ratio

$$k' = \frac{dP/dt}{(3P_0 - P)^\alpha} \quad (E5-1.7)$$

at any point.

3. Look for simplifications. We have assumed the reaction is reversible. Check to see if any terms in the equation can be neglected [e.g., the term ϵX in $(1 + \epsilon X)$ when $(\epsilon X \ll 1)$].

4. Determine dP/dt from the pressure-time data and then the reaction order α . The data are reported in terms of total pressure as a function of time; *consequently*, we must differentiate the data either numerically or graphically before we can use Equations (E5-1.6) and (E5-1.7) to evaluate the reaction order and specific reaction rate. First we shall evaluate dP/dt by graphical differentiation. Many prefer the graphical analysis because they use it to visualize the discrepancies in their data.

Graphical Method. The derivative dP/dt is determined by calculating and plotting $\Delta P/\Delta t$ as a function of time, t , and then using the equal-area differentiation technique (Appendix A.2) to determine (dP/dt) as a function of P and t . First we calculate the ratio $\Delta P/\Delta t$ from the first two columns of Table E5-1.2; the result is written in the third column. Next we use Table E5-1.2 to plot the third column as a function of the first column in Figure E5-1.1. Using equal-area differentiation, the value of dP/dt is read off the figure (represented by the arrows) and then it is used to complete the fourth column of Table E5-1.2.

TABLE E5-1.2. PROCESSED DATA

t (min)	P (mmHg)	$\frac{\Delta P}{\Delta t}$ (mmHg/min)	$\frac{dP}{dt}$ (mmHg/min)
0.0	7.5		1.44
2.5	10.5	1.20	0.95
5.0	12.5	0.80	0.74
10.0	15.8	0.66	0.53
15.0	17.9	0.42	0.34
20.0	19.4	0.30	0.25

Temperature = 170°C

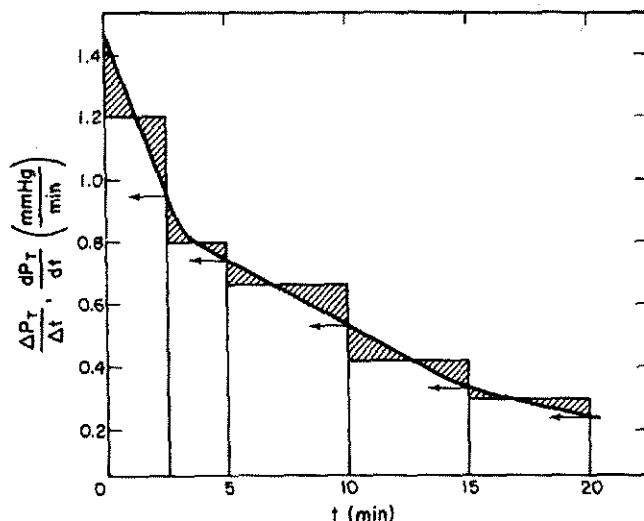


Figure E5-1.1 Graphical differentiation.

Finite Difference. Next we calculate dP/dt from finite difference formulas (5-8) through (5-10):

$$t = 0: \left(\frac{dP}{dt} \right)_0 = \frac{-3P_0 + 4P_1 - P_2}{2\Delta t} = \frac{-3(7.5) + 4(10.5) - 12.5}{2(2.5)} = 1.40$$

Calculating

$$t = 2.5: \left(\frac{dP}{dt} \right)_1 = \frac{P_2 - P_0}{2\Delta t} = \frac{12.5 - 7.5}{2(2.5)} = 1.0$$

$t = 5$: Here we have a change in time increments Δt , between P_1 and P_2 and between P_2 and P_3 . Consequently, we have two choices for evaluating $(dP/dt)_2$:

$$(a) \left(\frac{dP}{dt} \right)_2 = \frac{P_3 - P_0}{2(\Delta t)} = \frac{15.8 - 7.5}{2(5)} = 0.83$$

$$(b) \left(\frac{dP}{dt} \right)_2 = \frac{-3P_2 + 4P_3 - P_4}{2(\Delta t)} = \frac{-3(12.5) + 4(15.8) - 17.9}{2(5)} = 0.78$$

$$t = 10: \left(\frac{dP}{dt} \right)_3 = \frac{17.9 - 12.5}{2(5)} = 0.54$$

$$t = 15: \left(\frac{dP}{dt} \right)_4 = \frac{19.4 - 15.8}{2(5)} = 0.36$$

$$t = 20: \left(\frac{dP}{dt} \right)_5 = \frac{P_3 + 4P_4 - 3P_5}{2\Delta t} = \frac{15.8 - 4(17.9) + 3(19.4)}{2(5)} = 0.24$$

Polynomial (POLYMATH). Another method to determine dP/dt is to fit the total pressure to a polynomial in time and then to differentiate the resulting polynomial. Choosing a fourth-order polynomial

$$P = a_0 + a_1t + a_2t^2 + a_3t^3 + a_4t^4 \quad (E5-1.8)$$

we use the POLYMATH software package to express pressure as a function of time. Here we first choose the polynomial order (in this case fourth order) and then type in the values of P at various times t to obtain

$$P(t) = 7.53 + 1.31t - 0.0718t^2 + 0.00276t^3 - 4.83 \times 10^{-5}t^4 \quad (E5-1.9)$$

A plot of P versus t and the corresponding fourth-order polynomial fit is shown in Figure E5-1.2. Differentiating Equation (E5-1.9) yields

$$\frac{dP}{dt} = 1.31 - 0.144t + 0.00828t^2 - 0.000193t^3 \quad (E5-1.10)$$

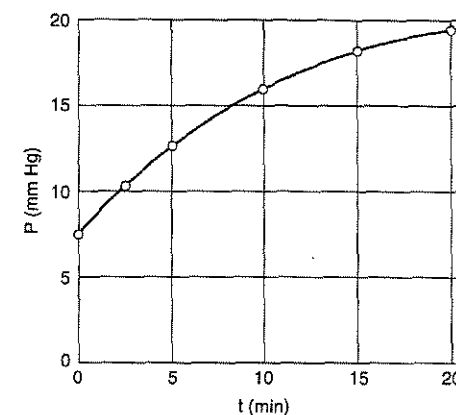
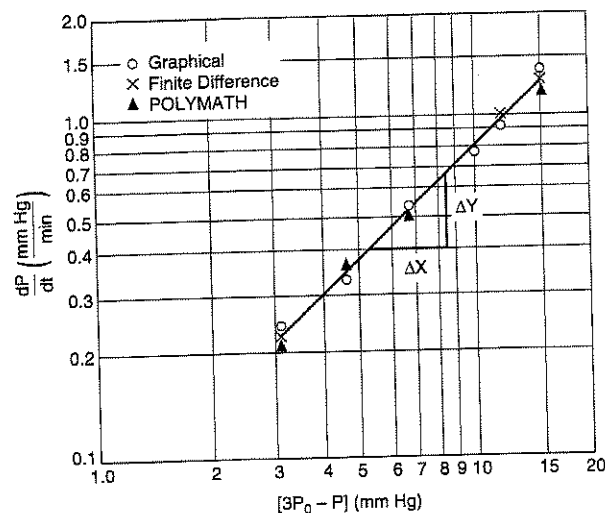


Figure E5-1.2 Polynomial fit.

To find the derivative at various times we substitute the appropriate time into Equation (E5-1.10) to arrive at the fourth column in Table E5-1.3. We can see that there is quite a close agreement between the graphical technique, finite difference, and the

TABLE E5-1.3. SUMMARY OF PROCESSED DATA

t (min)	dP/dt (mmHg/min) Graphical	dP/dt (mmHg/min) Finite Difference	dP/dt (mmHg/min) POLYMATH	$3P_0 - P$ (mmHg)
0.0	1.44	1.40	1.31	15.0
2.5	0.95	1.00	1.0	12.0
5.0	0.74	0.78	0.78	10.0
10.0	0.53	0.54	0.51	6.7
15.0	0.34	0.36	0.37	4.6
20.0	0.25	0.24	0.21	3.1

Figure E5-1.3. Plot to determine k and α .

POLYMATH polynomial analysis. The second, third, fourth, and fifth columns of the processed data in Table E5-1.3 are plotted in Figure E5-1.3 to determine the reaction order and specific reaction rate.

We shall determine the reaction order, α , from the slope of a log-log plot of dP/dt as a function of the appropriate function of pressure $f(P)$, which for the initial conditions and stoichiometry of this reaction turns out to be $(3P_0 - P)$ (see Table E5-1.3).³ Recall that

$$\ln \frac{dP}{dt} = \alpha \ln (3P_0 - P) + \ln k' \quad (\text{E5-1.6})$$

Using the line through the data points in Figure E5-1.3 yields

$$\alpha = \text{slope} = \frac{\Delta y}{\Delta x} = \frac{1.2 \text{ cm}}{1.2 \text{ cm}} = 1.0$$

The reaction order is

$$\alpha = 1.0$$

$$k' = k(2RT)^{1-\alpha} = k \quad (\text{E5-1.11})$$

$$-r_A = kC_A \quad (\text{E5-1.12})$$

³ If you are unfamiliar with any method of obtaining slopes from plots on log-log or semilog graphs, read Appendix D before proceeding.

Next, plot $\frac{dP}{dt}$ versus the appropriate function of total pressure

The integral method uses a trial-and-error procedure to find reaction order

It is important to know how to generate linear plots of C_A versus t for zero-, first-, and second-order reactions

5. Determine the specific reaction rate. The specific reaction rate can be determined using Equation (E5-1.7) with $\alpha = 1$ and then evaluating the numerator and denominator at any point, p .

$$k' = k = \frac{(dP/dt)_p}{(3P_0 - P)_p}$$

At $(3P_0 - P) = 5.0$ mmHg,

$$\frac{dP}{dt} = 0.4 \text{ mmHg/min}$$

From Equation (E5-1.5),

$$k = \left. \left(\frac{dP}{dt} \right)_p \right|_{(3P_0 - P)_p} = \frac{0.4 \text{ mmHg/min}}{5.0 \text{ mmHg}} = 0.08 \text{ min}^{-1}$$

The rate law is

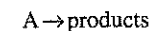
$$-r_A = \frac{0.08}{\text{min}} C_A \quad (\text{E5-1.13})$$

5.1.2 Integral Method

To determine the reaction order by the integral method, we guess the reaction order and integrate the differential equation used to model the batch system. If the order we assume is correct, the appropriate plot (determined from this integration) of the concentration-time data should be linear. The integral method is used most often when the reaction order is known and it is desired to evaluate the specific reaction rate constants at different temperatures to determine the activation energy.

In the integral method of analysis of rate data we are looking for the appropriate function of concentration corresponding to a particular rate law that is linear with time. You should be thoroughly familiar with the methods of obtaining these linear plots for reactions of zero, first, and second order.

For the reaction



carried out in a constant-volume batch reactor, the mole balance is

$$\frac{dC_A}{dt} = r_A$$

For a zero-order reaction, $r_A = -k$, and the combined rate law and mole balance is

$$\frac{dC_A}{dt} = -k \quad (5-13)$$

Integrating with $C_A = C_{A0}$ at $t = 0$, we have

Zero-order

$$C_A = C_{A0} - kt \quad (5-14)$$

A plot of the concentration of A as a function of time will be linear (Figure 5-3) with slope $(-k)$ for a zero-order reaction carried out in a constant-volume batch reactor.

$\alpha = 0$

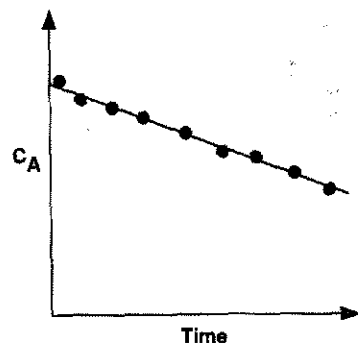


Figure 5-3 Zero-order reaction.

If the reaction is first order (Figure 5-4), integration of the combined mole balance and the rate law

$$-\frac{dC_A}{dt} = kC_A$$

with the limit $C_A = C_{A0}$ at $t = 0$ gives

First-order

$$\ln \frac{C_{A0}}{C_A} = kt \quad (5-15)$$

$\alpha = 1$

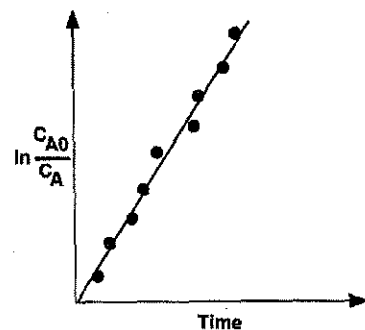


Figure 5-4 First-order reaction.

Consequently, we see that the slope of a plot of $[\ln(C_{A0}/C_A)]$ as a function of time is linear with slope k .

If the reaction is second order (Figure 5-5), then

$$-\frac{dC_A}{dt} = kC_A^2$$

Integrating with $C_A = C_{A0}$ initially yields

Second-order

$$\frac{1}{C_A} - \frac{1}{C_{A0}} = kt \quad (5-16)$$

$\alpha = 2$

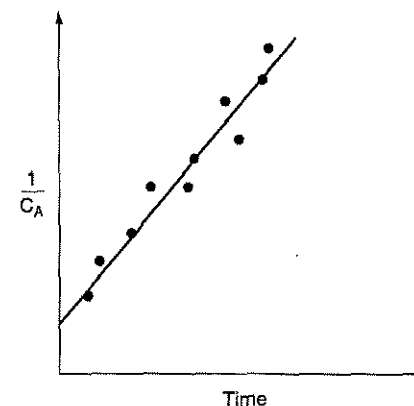


Figure 5-5 Second-order reaction.

We see that for a second-order reaction a plot of $1/C_A$ as a function of time should be linear with slope k .

In the three figures just discussed, we saw that when we plotted the appropriate function of concentration (i.e., C_A , $\ln C_A$ or $1/C_A$) versus time, the plots were linear and we concluded that the reactions were zero, first, or second order, respectively. However, if the plots of concentration data versus time had turned out not to be linear such as shown in Figure 5-6, we would say that the proposed reaction order did not fit the data. In the case of Figure 5-6, we would conclude the reaction is not second order.

It is important to restate that given a reaction rate law, you should be able to choose quickly the appropriate function of concentration or conversion that yields a straight line when plotted against time or space time.

The idea is to arrange the data so that a linear relationship is obtained

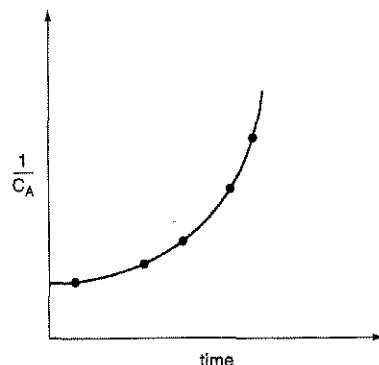
$\alpha \neq 2$ 

Figure 5-6 Plot of reciprocal concentration as a function of time.

Example 5-2 Integral Method of Analysis of Pressure-Time Data

Use the integral method to confirm that the reaction order for the di-*tert*-butyl peroxide decomposition described in Example 5-1 is first order.

Solution

Recalling Example 5-1, the combined mole balance and rate law for a constant-volume batch reactor can be expressed in the form

$$\frac{dP}{dt} = k'(3P_0 - P)^\alpha \quad (\text{E5-1.7})$$

For $\alpha = 1$,

$$\frac{dP}{dt} = k'(3P_0 - P) \quad (\text{E5-2.1})$$

Integrating with limits $P = P_0$ when $t = 0$ yields

$$\ln \frac{2P_0}{3P_0 - P} = k't \quad (\text{E5-2.2})$$

If the reaction is first order, a plot of $\ln[2P_0/(3P_0 - P)]$ versus t should be linear.

TABLE E5-2.1. PROCESSED DATA

t (min)	P (mmHg)	$2P_0/(3P_0 - P)$ (—)
0.0	7.5	1.00
2.5	10.5	1.25
5.0	12.5	1.50
10.0	15.8	2.24
15.0	17.9	3.26
20.0	19.4	4.84

After completing Table E5-2.1, using the raw data, a plot of $2P_0/(3P_0 - P)$ as a function of time was made using semilog paper as shown in Figure E5-2.1. From

Assuming a first-order reaction

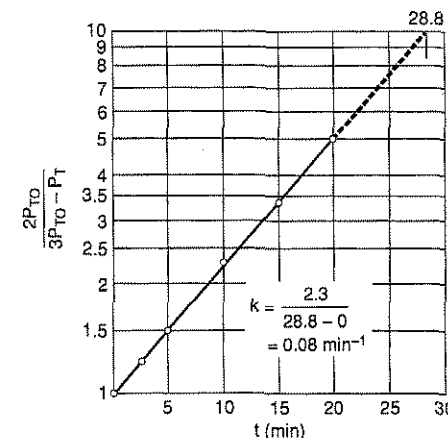


Figure E5-2.1 Plot of processed data.

the plot we see that $\ln[2P_0/(3P_0 - P)]$ is indeed linear with time, and we therefore conclude that the decomposition of di-*tert*-butyl peroxide follows first-order kinetics. From the slope of the plot in Figure E5-2.1, we can determine the specific reaction rate, $k = 0.08 \text{ min}^{-1}$. [Recall $k' = k$ because $\alpha = 1$ (E5-1.5 p. 230)]

We found the plot of $\ln[2P_0/(3P_0 - P)]$ versus t was linear, indicating that the reaction is first order (i.e., $\alpha = 1$). If we try zero, first, or second order as shown on the CD-ROM, and they do not seem to describe the reaction rate equation, it is usually best to try some other method of determining the reaction order, such as the differential method.



Integral method normally used to find k when order is known

By comparing the methods of analysis of the rate data presented above, we note that the differential method tends to accentuate the uncertainties in the data, while the integral method tends to smooth the data, thereby disguising the uncertainties in it. In most analyses it is imperative that the engineer know the limits and uncertainties in the data. This prior knowledge is necessary to provide for a safety factor when scaling up a process from laboratory experiments to design either a pilot plant or full-scale industrial plant.

5.2 Method of Initial Rates

The use of the differential method of data analysis to determine reaction orders and specific reaction rates is clearly one of the easiest, since it requires only one experiment. However, other effects, such as the presence of a significant reverse reaction, could render the differential method ineffective. In these cases, the method of initial rates could be used to determine the reaction order and the specific rate constant. Here, a series of experiments is carried out at different initial concentrations, C_{A0} , and the initial rate of reaction, $-r_{A0}$, is determined for each run. The initial rate, $-r_{A0}$, can be found by differentiating the data and extrapolating to zero time. For example, in the di-*tert*-butyl peroxide decomposition shown in Example 5-1, the initial rate was found to be

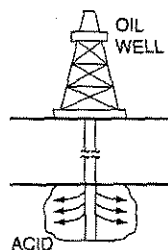
Used when reactions are reversible

1.4 mmHg/min. By various plotting or numerical analysis techniques relating $-r_{A0}$ to C_{A0} , we can obtain the appropriate rate law. If the rate law is in the form

$$-r_{A0} = kC_{A0}^{\alpha}$$

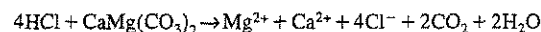
the slope of the plot of $\ln(-r_{A0})$ versus $\ln C_{A0}$ will give the reaction order α .

Example 5-3 Method of Initial Rates in Solid-Liquid Dissolution Kinetics



An important reaction for enhancement of oil flow in carbonate reservoirs

The dissolution of dolomite, calcium magnesium carbonate, in hydrochloric acid is a reaction of particular importance in the acid stimulation of dolomite oil reservoirs.⁴ The oil is contained in pore space of the carbonate material and must flow through the small pores to reach the well bore. In matrix stimulation, HCl is injected into a well bore to dissolve the porous carbonate matrix. By dissolving the solid carbonate the pores will increase in size, and the oil and gas will be able to flow out at faster rates, thereby increasing the productivity of the well.⁵ The dissolution reaction is



The concentration of HCl at various times was determined from atomic absorption spectrophotometer measurements of the calcium and magnesium ions.

Determine the reaction order with respect to HCl from the data presented in Figure E5-3.1 for this batch reaction. Assume that the rate law is in the form given by Equation (5-1) and that the combined rate law and mole balance for HCl can be given by Equation (5-6).

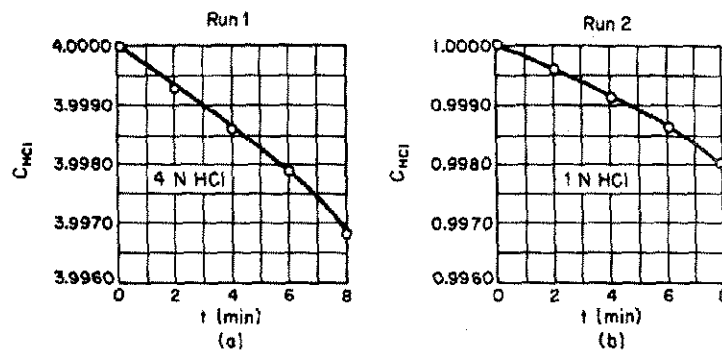


Figure E5-3.1 Concentration-time data.

Solution

Evaluating the mole balance on a constant-volume batch reactor at time $t = 0$ gives

$$\left(-\frac{dC_{\text{HCl}}}{dt}\right)_0 = -(r_{\text{HCl}})_0 = kC_{\text{HCl},0}^{\alpha} \quad (\text{E5-3.1})$$

⁴ K. Lund, H. S. Fogler, and C. C. McCune, *Chem. Eng. Sci.*, 28, 691 (1973).

⁵ M. Hoefner and H. S. Fogler, *AIChE Journal*, 34(1), 45 (1988).

Taking the log of both sides of Equation (E5-3.1), we have

$$\ln\left(-\frac{dC_{\text{HCl}}}{dt}\right)_0 = \ln k + \alpha \ln C_{\text{HCl},0} \quad (\text{E5-3.2})$$

The derivative at time $t = 0$ can be found from the slope of the plot of concentration versus time evaluated at $t = 0$. Figure E5-3.1(a) and (b) give

4 N HCl solution	1 N HCl solution
$-r_{\text{HCl},0} = -\frac{3.9982 - 4.0000}{5 - 0}$	$-r_{\text{HCl},0} = -\frac{0.9987 - 1.0000}{6 - 0}$
$-r_{\text{HCl},0} = 3.6 \times 10^{-4} \text{ g mol/L} \cdot \text{min}$	$-r_{\text{HCl},0} = 2.2 \times 10^{-4} \text{ g mol/L} \cdot \text{min}$

Converting to a rate per unit area, $-r_A'$, and to seconds (30 cm² of solid per liter of solution), the rates at 1 N and 4 N become $1.2 \times 10^{-7} \text{ mol/cm}^2 \cdot \text{s}$ and $2.0 \times 10^{-7} \text{ mol/cm}^2 \cdot \text{s}$, respectively. We also could have used either POLYMATH or the differentiation formulas to find the derivative at $t = 0$.

If we were to continue in this manner, we would generate the following data set.⁶

TABLE 5-3.

$C_{\text{HCl},0} \text{ (mol/cm}^3\text{)}$	1.0	4.0	2.0	0.1	0.5
$-r_{\text{HCl},0}' \text{ (mol/cm}^2 \cdot \text{s)} \times 10^7$	1.2	2.0	1.36	0.36	0.74

These data are plotted on Figure E5-3.2. The slope of this \ln - \ln plot of $-r_{\text{HCl},0}'$ versus $C_{\text{HCl},0}$ shown in Figure E5-3.2 gives a reaction order of 0.44. The rate law is

$$-r_{\text{HCl},0}' = kC_{\text{HCl}}^{0.44} \quad (\text{E5-3.3})$$

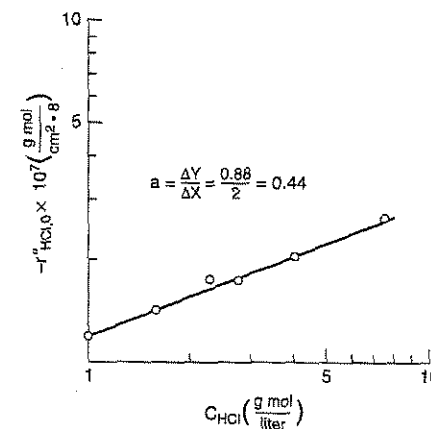


Figure E5-3.2 Initial rate as a function of initial HCl concentration.

⁶ K. Lund, H. S. Fogler, and C. C. McCune, *Chem. Eng. Sci.*, 28, 691 (1973).

For this dissolution of dolomite in HCl, the reaction order was also found to vary with temperature.

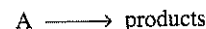
5.3 Method of Half-Lives

The method of half-lives requires many experiments

The half-life of a reaction, $t_{1/2}$, is defined as the time it takes for the concentration of the reactant to fall to half of its initial value. By determining the half-life of a reaction as a function of the initial concentration, the reaction order and specific reaction rate can be determined. If two reactants are involved in the chemical reaction, the experimenter will use the method of excess in conjunction with the method of half-lives to arrange the rate law in the form

$$-r_A = kC_A^\alpha \quad (5-1)$$

For the irreversible reaction



a mole balance on species A in a constant-volume batch reaction system results in the following expression:

$$-\frac{dC_A}{dt} = -r_A = kC_A^\alpha \quad (E5-1.1)$$

Integrating with the initial condition $C_A = C_{A0}$ when $t = 0$, we find that

$$\begin{aligned} t &= \frac{1}{k(\alpha-1)} \left(\frac{1}{C_A^{\alpha-1}} - \frac{1}{C_{A0}^{\alpha-1}} \right) \\ &= \frac{1}{kC_{A0}^{\alpha-1}(\alpha-1)} \left[\left(\frac{C_{A0}}{C_A} \right)^{\alpha-1} - 1 \right] \end{aligned} \quad (5-17)$$

The half-life is defined as the time required for concentration to drop to half of its initial value; that is,

$$t = t_{1/2} \quad \text{when} \quad C_A = \frac{1}{2} C_{A0}$$

Substituting for C_A in Equation (5-17) gives us

$$t_{1/2} = \frac{2^{\alpha-1} - 1}{k(\alpha-1)} \left(\frac{1}{C_{A0}^{\alpha-1}} \right) \quad (5-18)$$

There is nothing special about using the time required for the concentration to drop to one-half of its initial value. We could just as well use the time required for the concentration to fall to $1/n$ of the initial value, in which case

$$t_{1/n} = \frac{n^{\alpha-1} - 1}{k(\alpha-1)} \left(\frac{1}{C_{A0}^{\alpha-1}} \right) \quad (5-19)$$

For the method of half-lives, taking the natural log of both sides of Equation (5-18),

$$\ln t_{1/2} = \ln \frac{2^{\alpha-1} - 1}{(\alpha-1)k} + (1-\alpha) \ln C_{A0}$$

we see that the slope of the plot of $\ln t_{1/2}$ as a function of $\ln C_{A0}$ is equal to 1 minus the reaction order:

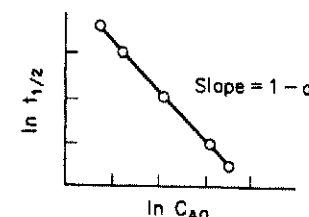


Figure 5-7 Method of half-lives.

Rearranging:

$$\alpha = 1 - \text{slope}$$

For the plot shown in Figure 5-7 the slope is -1 :

$$\alpha = 1 - (-1) = 2$$

The corresponding rate law is

$$-r_A = kC_A^2$$

5.4 Differential Reactors

Data acquisition using the method of initial rates and a differential reactor are similar in that the rate of reaction is determined for a specified number of predetermined initial or entering reactant concentrations. A differential reactor is normally used to determine the rate of reaction as a function of either concentration or partial pressure. It consists of a tube containing a very small amount of catalyst usually arranged in the form of a thin wafer or disk. A typical arrangement is shown schematically in Figure 5-8. The criterion for a reactor being differential is that the conversion of the reactants in the bed is extremely small, as is the change in reactant concentration through the bed. As a result, the reactant concentration through the reactor is essentially constant and approximately equal to the inlet concentration. That is, the reactor is considered to be gradientless,⁷ and the reaction rate is considered spatially uniform within the bed.

⁷ B. Anderson, ed., *Experimental Methods in Catalytic Research* (San Diego, Calif.: Academic Press, 1968).

Plot $t_{1/2}$ as a function of C_{A0} or use regression software

Most commonly
used catalytic
reactor to obtain
experimental data

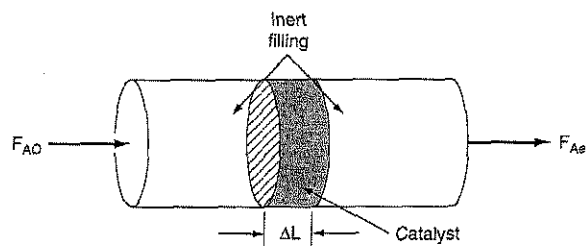


Figure 5-8 Differential reactor.

The differential reactor is relatively easy to construct at a low cost. Owing to the low conversion achieved in this reactor, the heat release per unit volume will be small (or can be made small by diluting the bed with inert solids) so that the reactor operates essentially in an isothermal manner. When operating this reactor, precautions must be taken so that the reactant gas or liquid does not bypass or channel through the packed catalyst, but instead flows uniformly across the catalyst. If the catalyst under investigation decays rapidly, the differential reactor is not a good choice because the reaction rate parameters at the start of a run will be different from those at the end of the run. In some cases sampling and analysis of the product stream may be difficult for small conversions in multicomponent systems.

The volumetric flow rate through the catalyst bed is monitored, as are the entering and exiting concentrations (Figure 5-9). Therefore, if the weight of

Limitations of the
differential reactor

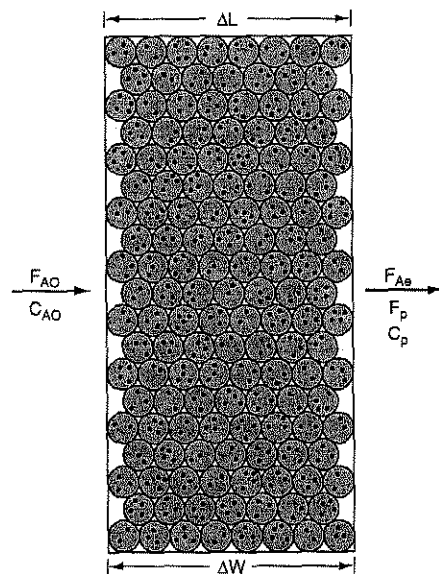


Figure 5-9 Differential catalyst bed.

catalyst, W , is known, the rate of reaction per unit mass of catalyst, r'_A , can be calculated. Since the differential reactor is assumed to be *gradientless*, the design equation will be similar to the CSTR design equation. A steady-state mole balance on reactant A gives

$$\left[\begin{array}{c} \text{flow} \\ \text{rate} \\ \text{in} \end{array} \right] - \left[\begin{array}{c} \text{flow} \\ \text{rate} \\ \text{out} \end{array} \right] + \left[\begin{array}{c} \text{rate of} \\ \text{generation} \end{array} \right] = \left[\begin{array}{c} \text{rate of} \\ \text{accumulation} \end{array} \right]$$

$$[F_{A0}] - [F_{Ae}] + \left[\left(\frac{\text{rate of reaction}}{\text{mass of cat.}} \right) (\text{mass of cat.}) \right] = 0$$

$$F_{A0} - F_{Ae} + (r'_A)(W) = 0$$

The subscript e refers to the exit of the reactor. Solving for $-r'_A$, we have

$$-r'_A = \frac{F_{A0} - F_{Ae}}{W} \quad (5-20)$$

The mole balance equation can also be written in terms of the concentration

$$-r'_A = \frac{v_0 C_{A0} - v C_{Ae}}{W} \quad (5-21)$$

or in terms of the conversion or product flow rate F_P :

$$-r'_A = \frac{F_{A0}X}{W} = \frac{F_P}{W} \quad (5-22)$$

The term $F_{A0}X$ gives the rate of formation of the product, F_P , when the stoichiometric coefficients of A and of P are identical.

For constant volumetric flow, Equation (5-21) reduces to

$$-r'_A = \frac{v_0(C_{A0} - C_{Ae})}{W} = \frac{v_0 C_P}{W} \quad (5-23)$$

Consequently, we see that the reaction rate, $-r'_A$, can be determined by measuring the product concentration, C_P .

By using very little catalyst and large volumetric flow rates, the concentration difference, $(C_{A0} - C_{Ae})$, can be made quite small. The rate of reaction determined from Equation (5-23) can be obtained as a function of the reactant concentration in the catalyst bed, C_{Ab} :

$$-r'_A = -r'_A(C_{Ab}) \quad (5-24)$$

by varying the inlet concentration. One approximation of the concentration of A within the bed, C_{Ab} , would be the arithmetic mean of the inlet and outlet concentrations:

$$C_{Ab} = \frac{C_{A0} + C_{Ae}}{2} \quad (5-25)$$

However, since very little reaction takes place within the bed, the bed concentration is essentially equal to the inlet concentration,

$$C_{Ab} \approx C_{A0}$$

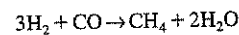
so $-r'_A$ is a function of C_{A0} :

$$-r'_A = -r'_A(C_{A0}) \quad (5-26)$$

As with the method of initial rates, various numerical and graphical techniques can be used to determine the appropriate algebraic equation for the rate law.

Example 5-4 Differential Reactor

The formation of methane from carbon monoxide and hydrogen using a nickel catalyst was studied by Pursley.⁸ The reaction



was carried out at 500°F in a differential reactor where the effluent concentration of methane was measured.

(a) Relate the rate of reaction to the exit methane concentration.

(b) The reaction rate law is assumed to be the product of a function of the partial pressure of CO, $f(\text{CO})$, and a function of the partial pressure of H_2 , $g(\text{H}_2)$:

$$r'_{\text{CH}_4} = f(\text{CO}) \cdot g(\text{H}_2) \quad (\text{E5-4.1})$$

Determine the reaction order with respect to carbon monoxide, using the data in Table E5-4.1. Assume that the functional dependence of r'_{CH_4} on P_{CO} is of the form

$$r'_{\text{CH}_4} \sim P_{\text{CO}}^\alpha \quad (\text{E5-4.2})$$

TABLE E5-4.1 RAW DATA

Run	P_{CO} (atm)	P_{H_2} (atm)	C_{CH_4} (g mol/dm ³)
1	1	1.0	2.44×10^{-4}
2	1.8	1.0	4.40×10^{-4}
3	4.08	1.0	10.0×10^{-4}
4	1.0	0.1	1.65×10^{-4}
5	1.0	0.5	2.47×10^{-4}
6	1.0	4.0	1.75×10^{-4}

P_{H_2} is constant in
Runs 1, 2, 3
 P_{CO} is constant in
Runs 4, 5, 6

⁸ J. A. Pursley, An Investigation of the Reaction between Carbon Monoxide and Hydrogen on a Nickel Catalyst above One Atmosphere, Ph.D. thesis, University of Michigan.

The exit volumetric flow rate from a differential packed bed containing 10 g of catalyst was maintained at 300 dm³/min for each run. The partial pressures of H_2 and CO were determined at the entrance to the reactor, and the methane concentration was measured at the reactor exit.

Solution

(a) In this example the product composition, rather than the reactant concentration, is being monitored. $-r'_A$ can be written in terms of the flow rate of methane from the reaction,

$$-r'_A = r'_{\text{CH}_4} = \frac{F_{\text{CH}_4}}{\Delta W}$$

Substituting for F_{CH_4} in terms of the volumetric flow rate and the concentration of methane gives

$$-r'_A = \frac{v_0 C_{\text{CH}_4}}{\Delta W} \quad (\text{E5-4.3})$$

Since v_0 , C_{CH_4} , and ΔW are known for each run, we can calculate the rate of reaction. For run 1:

$$-r'_A = \left(\frac{300 \text{ dm}^3}{\text{min}} \right) \frac{2.44 \times 10^{-4}}{10 \text{ g cat.}} \text{ g mol/dm}^3 = 7.33 \times 10^{-3} \frac{\text{g mol CH}_4}{\text{g cat.} \times \text{min}}$$

The rate for runs 2 through 6 can be calculated in a similar manner (Table E5-4.2).

TABLE E5-4.2 RAW AND CALCULATED DATA

Run	P_{CO} (atm)	P_{H_2} (atm)	C_{CH_4} (g mol/dm ³)	r'_{CH_4} $\left(\frac{\text{g mol CH}_4}{\text{g cat.} \times \text{min}} \right)$
1	1.0	1.0	2.44×10^{-4}	7.33×10^{-3}
2	1.8	1.0	4.40×10^{-4}	13.2×10^{-3}
3	4.08	1.0	10.0×10^{-4}	30.0×10^{-3}
4	1.0	0.1	1.65×10^{-4}	4.95×10^{-3}
5	1.0	0.5	2.47×10^{-4}	7.42×10^{-3}
6	1.0	4.0	1.75×10^{-4}	5.25×10^{-3}

For constant hydrogen concentration, the rate law

$$r'_{\text{CH}_4} = k P_{\text{CO}}^\alpha \cdot g(P_{\text{H}_2})$$

can be written as

$$r'_{\text{CH}_4} = k' P_{\text{CO}}^\alpha \quad (\text{E5-4.4})$$

Taking the log of Equation (E5-4.4) gives us

$$\ln(r'_{\text{CH}_4}) = \ln k' + \alpha \ln P_{\text{CO}}$$

We now plot $\ln(r'_{\text{CH}_4})$ versus $\ln P_{\text{CO}}$ for runs 1, 2, and 3.

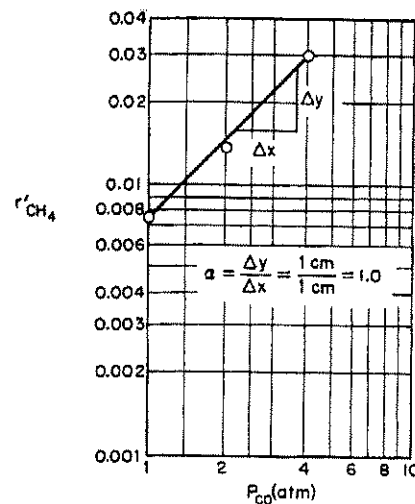


Figure E5-4.1 Reaction rate as a function of partial pressure.

(b) Runs 1, 2, and 3, for which the H_2 concentration is constant, are plotted in Figure E5-4.1. From the slope of the plot in Figure E5-4.1, we find that $\alpha = 1$.

$$-r'_A = k' P_{CO} \quad (E5-4.5)$$

Determining the Rate Law Dependence on H_2

From Table E5-4.2 it appears that the dependence of $-r'_{CH_4}$ on P_{H_2} cannot be represented by a power law. Comparing run 4 with run 5 and run 1 with run 6, we see that the reaction rate first increases with increasing partial pressure of hydrogen, and subsequently decreases with increasing P_{H_2} . That is, there appears to be a concentration of hydrogen at which the rate is maximum. One set of rate laws that is consistent with these observations is:

1. At low H_2 concentrations where r'_{CH_4} increases as P_{H_2} increases, the rate law may be of the form

$$r'_{CH_4} \sim P_{H_2}^{\beta_1} \quad (E5-4.6)$$

2. At high H_2 concentrations where r'_{CH_4} decreases as P_{H_2} increases,

$$r'_{CH_4} \sim \frac{1}{P_{H_2}^{\beta_2}} \quad (E5-4.7)$$

We would like to find one rate law that is consistent with reaction rate data at both high and low hydrogen concentrations. Experience suggests Equations (E5-4.6) and (E5-4.7) can be combined into the form

$$r'_{CH_4} \sim \frac{P_{H_2}^{\beta_1}}{1 + bP_{H_2}^{\beta_2}} \quad (E5-4.8)$$

Typical form of the rate law for heterogeneous catalysis

Sec. 5.4 Differential Reactors

We will see in Chapter 10 that this combination and similar rate laws which have reactant concentrations (or partial pressures) in the numerator and denominator are common in *heterogeneous catalysis*.

Let's see if the resulting rate law (E5-4.8) is qualitatively consistent with the rate observed.

1. For condition 1: At low P_{H_2} , $b((P_{H_2})^{\beta_2}) \ll 1$ and Equation (E5-4.8) reduces to

$$r'_{CH_4} \sim P_{H_2}^{\beta_1} \quad (E5-4.9)$$

Equation (E5-4.9) is consistent with the trend in comparing runs 4 and 5.

2. For condition 2: At high P_{H_2} , $b((P_{H_2})^{\beta_2}) \gg 1$ and Equation (E5-4.8) reduces to

$$r'_{CH_4} \sim \frac{(P_{H_2})^{\beta_1}}{(P_{H_2})^{\beta_2}} \sim \frac{1}{(P_{H_2})^{\beta_2 - \beta_1}} \quad (E5-4.10)$$

where $\beta_2 > \beta_1$. Equation (E5-4.10) is consistent with the trends in comparing runs 5 and 6.

Theoretical considerations of the type to be discussed in Chapter 10 predict that if the rate-limiting step in the overall reaction is the reaction between atomic hydrogen absorbed on the nickel surface and CO in the gas phase, then the rate law will be in the form

$$r'_{CH_4} = \frac{aP_{CO}P_{H_2}^{1/2}}{1 + bP_{H_2}} \quad (E5-4.11)$$

This rate law is qualitatively consistent with experimental observations. To obtain the parameter a and b , we rearrange Equation (E5-4.11) in the form

$$\frac{P_{CO}P_{H_2}^{1/2}}{r'_{CH_4}} = \frac{1}{a} + \frac{b}{a}P_{H_2} \quad (E5-4.12)$$

A plot of $P_{CO}P_{H_2}^{1/2}/r'_{CH_4}$ as a function of P_{H_2} should be a straight line with an intercept of $1/a$ and a slope of b/a . From the plot in Figure E5-4.2 we see that the rate law is indeed consistent with the rate law data.

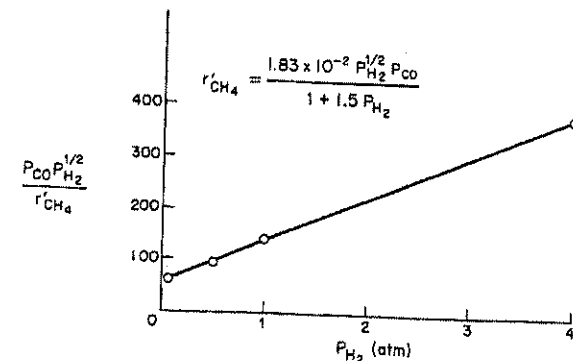


Figure E5-4.2 Linearizing plot of data.

As an exercise, use the analysis in section 5.5 to find the rate law shown in Figure E5-4.2.

Linearizing the rate law to determine the rate law parameters

5.5 Least-Squares Analysis

5.5.1 Linearization of the Rate Law

If a rate law depends on the concentration of more than one species and it is not possible to use the method of excess, we may choose to use a linearized least-squares method. This method of data analysis is also useful to determine the best values of the rate law parameters from a series of measurements when three or more parameters are involved (e.g., reaction order, α ; frequency factor, A ; and activation energy, E).

A mole balance on a constant-volume batch reactor gives

$$-\frac{dC_A}{dt} = -r_A = kC_A^\alpha C_B^\beta \quad (5-27)$$

If we now use the method of initial rates, then

$$\left(-\frac{dC_A}{dt}\right)_0 = -r_{A0} = kC_{A0}^\alpha C_{B0}^\beta$$

Taking the log of both sides, we have

$$\ln\left(-\frac{dC_A}{dt}\right)_0 = \ln k + \alpha \ln C_{A0} + \beta \ln C_{B0} \quad (5-28)$$

Used when C_{A0} and C_{B0} are varied simultaneously

Let $Y = \ln(-dC_A/dt)_0$, $X_1 = \ln C_{A0}$, $X_2 = \ln C_{B0}$, $a_0 = \ln k$, $a_1 = \alpha$, and $a_2 = \beta$. Then

$$Y = a_0 + a_1 X_1 + a_2 X_2 \quad (5-29)$$

If we now carry out N experimental runs, for the j th run, Equation (5-29) takes the form

$$Y_j = a_0 + a_1 X_{1j} + a_2 X_{2j} \quad (5-30)$$

where $X_{1j} = \ln C_{A0j}$, with C_{A0j} being the initial concentration of A for the j th run. The best values of the parameters a_0 , a_1 , and a_2 are found by solving Equations (5-31) through (5-33) simultaneously.

For N runs, 1, 2, ..., N ,

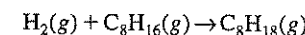
$$\sum_{j=1}^N Y_j = Na_0 + a_1 \sum_{j=1}^N X_{1j} + a_2 \sum_{j=1}^N X_{2j} \quad (5-31)$$

$$\sum_{j=1}^N X_{1j} Y_j = a_0 \sum_{j=1}^N X_{1j} + a_1 \sum_{j=1}^N X_{1j}^2 + a_2 \sum_{j=1}^N X_{1j} X_{2j} \quad (5-32)$$

$$\sum_{j=1}^N X_{2j} Y_j = a_0 \sum_{j=1}^N X_{2j} + a_1 \sum_{j=1}^N X_{1j} X_{2j} + a_2 \sum_{j=1}^N X_{2j}^2 \quad (5-33)$$

Three equations,
three unknowns
(a_0, a_1, a_2)

We have three linear equations and three unknowns which we can solve for: a_0 , a_1 , and a_2 . A detailed example delineating the kinetics of the reaction



using linear least-squares analysis can be found in Example 10-2. If we set $a_2 = 0$ and consider only two variables, Y and X , Equations (5-31) and (5-32) reduce to the familiar least-squares equations for two unknowns.

Example 5-5 Using Least-Squares Analysis to Determine Rate Law Parameters

The etching of semiconductors in the manufacture of computer chips is another important solid-liquid dissolution reaction (see Problem P5-12 and Section 12.10). The dissolution of the semiconductor MnO_2 was studied using a number of different acids and salts. The rate of dissolution was found to be a function of the reacting liquid solution redox potential relative to the energy-level conduction band of the semiconductor. It was found that the reaction rate could be increased by a factor of 10^5 simply by changing the anion of the acid⁹!! From the data below, determine the reaction order and specific reaction rate for the dissolution of MnO_2 in HBr .

C_{A0} (mol HBr/dm^3)	0.1	0.5	1.0	2.0	4.0
$-r_{A0}'$ (mol $\text{HBr}/\text{m}^2 \cdot \text{h}) \times 10^2$	0.073	0.70	1.84	4.86	12.84

Solution

We assume a rate law of the form

$$-r_{\text{HBr}}' = kC_{\text{HBr}}^\alpha \quad (\text{E5-5.1})$$

Letting $A = \text{HBr}$, taking the \ln of both sides of (E5-5.1), and using the initial rate and concentration gives

$$\ln(-r_{A0}') = \ln k + \alpha \ln C_{A0} \quad (\text{E5-5.2})$$

Let $Y = \ln(-r_{A0}')$, $a = \ln k$, $b = \alpha$, and $X = \ln C_{A0}$. Then

$$Y = a + bX \quad (\text{E5-5.3})$$

The least-squares equations to be solved for the best values of a and b are for N runs

$$\sum_{i=1}^N Y_i = Na + b \sum_{i=1}^N X_i \quad (\text{E5-5.4})$$

$$\sum_{i=1}^N X_i Y_i = a \sum_{i=1}^N X_i + b \sum_{i=1}^N X_i^2 \quad (\text{E5-5.5})$$

where i = run number. Substituting the appropriate values from Table E5-5.1 into Equations (E5-5.4) and (E5-5.5) gives

$$-21.26 = 5a + -0.92b \quad (\text{E5-5.6})$$

$$15.10 = -0.92a + 8.15b \quad (\text{E5-5.7})$$

⁹ S. E. Le Blanc and H. S. Fogler, *AIChE J.*, 32, 1702 (1986).

TABLE E5-5.1

Run	C_{A0}	X_i	$-r_{A0}''$	Y_i	$X_i Y_i$	X_i^2
1	0.1	-2.302	0.00073	-7.22	16.61	5.29
2	0.5	-0.693	0.007	-4.96	3.42	0.48
3	1.0	0.0	0.0184	-4.0	0.0	0.0
4	2.0	0.693	0.0486	-3.02	-2.09	0.48
5	4.0	1.38	0.128	-2.06	-2.84	1.90
		$\sum_{i=1}^5 X_i = -0.92$			$\sum_{i=1}^5 Y_i = -21.26$	$\sum_{i=1}^5 X_i Y_i = 15.1$
					$\sum_{i=1}^5 X_i^2 = 8.15$	

Solving for a and b yields

$$b = 1.4 \quad \text{therefore} \quad \alpha = 1.4$$

and

$$a = -3.99 \quad k = 1.84 \times 10^{-2} (\text{dm}^3/\text{mol})^{0.4}/\text{m}^2 \cdot \text{h}$$

$$r_{\text{HBr}}'' = 0.0184 C_{\text{HBr}}^{1.4} \quad (\text{E5-5.8})$$

5.5.2 Nonlinear Least-Squares¹⁰ Analysis

In nonlinear least squares analysis we search for those parameter values that minimize the sum of squares of the differences between the measured values and the calculated values for all the data points. Many software programs are available to find these parameter values and all one has to do is to enter the data. The POLYMATH software will be used to illustrate this technique. In order to carry out the search efficiently, in some cases one has to enter initial estimates of the parameter values close to the actual values. These estimates can be obtained using the linear-least-squares technique just discussed.

We will now apply nonlinear least-squares analysis to reaction rate data to determine the rate law parameters. Here we make estimates of the parameter values (e.g., reaction order, specific rate constants) in order to calculate the rate of reaction, r_c . We then search for those values that will minimize the sum of the squared differences of the measured reaction rates, r_m , and the calculated reaction rates, r_c . That is, we want the sum of $(r_m - r_c)^2$ for all data points to be minimum. If we carried out N experiments, we would want to find the parameter values (e.g., E , activation energy, reaction orders) that would minimize the quantity

$$\sigma^2 = \frac{s^2}{N - K} = \frac{\sum_{i=1}^N (r_{im} - r_{ic})^2}{N - K} \quad (\text{E5-34})$$

¹⁰See also R. Mezakiki and J. R. Kittrell, *AIChE J.*, 14, 513 (1968), and J. R. Kittrell, *Ind. Eng. Chem.*, 61, (5), 76-78 (1969).

where

$$s^2 = \sum (r_{im} - r_{ic})^2$$

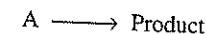
N = number of runs

K = number of parameters to be determined

r_{im} = measured reaction rate for run i (i.e., $-r_{Aim}$)

r_{ic} = calculated reaction rate for run i (i.e., $-r_{Aic}$)

To illustrate this technique, let's consider the first-order reaction



for which we want to learn the reaction order, α , and the specific reaction rate, k ,

$$r = kC_A^\alpha$$

The reaction rate will be measured at a number of different concentrations and these measurements are shown on the left of Table 5-2.

We now choose values of k and α and calculate the rate of reaction (r_{ic}) at each concentration at which an experimental point was taken. We then subtract the calculated value from the measured value (r_{im}), square the result, and sum the squares for all the runs for the values of k and α we have chosen. For example, consider the data set given for runs 1 through 4 in the second and third columns. In trial 1 we first guess $k = 1$ and $\alpha = 1$ and then calculate the rate based on these values. For run 1 the calculated value of the rate is $r_i = (1)(0.6)^1 = 0.6$. The difference between the measured rate and the calculated rate is $r_{im} - r_{ic} = 1.9 - 0.6 = 1.3$. The squared difference $(r_{im} - r_{ic})^2$ is 1.69. We make similar calculations for runs 2 through 4 and they are shown in the sixth column. Next we sum up all the squared differences [$s^2 = \sum_1^4 (r_{im} - r_{ic})^2$] for all the runs and obtain $s^2 = 114.04$ for the values chosen: $\alpha = 1$, $k = 1$. Next choose new values of α and k . In the seventh and eighth columns the calculated rate and the differences $(r_{im} - r_{ic})^2$ are given for $\alpha = 1$, $k = 4$. Next, new values for k and α are chosen and the procedure is repeated. Initial estimates of k and α can be obtained by a linearized least-squares analysis. Table 5-2 shows an example of how the sum of the squares (σ_1^2 and σ_2^2) is calculated for N .

Finding values of α and k to minimize σ^2

TABLE 5-2. MINIMIZING THE SUM OF THE SQUARE DIFFERENCES

Data			Trial 1 $k = 1, \alpha = 1$			Trial 2 $k = 4, \alpha = 1$		Trial 3 $k = 4, \alpha = 1.5$		Trial 4 $k = 5, \alpha = 1.5$		Trial 5 $k = 5, \alpha = 2$	
Run	C_A	r_m	r_c	$r_m - r_c$	$(r_m - r_c)^2$	r_c	$(r_m - r_c)^2$	r_c	$(r_m - r_c)^2$	r_c	$(r_m - r_c)^2$	r_c	$(r_m - r_c)^2$
1	0.6	1.9	0.6	1.3	1.69	2.4	0.25	1.86	0.0016	2.32	0.18	1.80	0.01
2	0.8	3.1	0.8	2.3	5.29	3.2	0.01	2.86	0.06	3.58	0.23	3.2	0.01
3	1.0	5.1	1.0	4.1	16.81	4.0	1.21	4.0	1.21	5.0	0.01	5.0	0.01
4	1.5	11.0	1.5	9.5	90.25	6.0	25.0	7.35	13.32	9.19	3.28	11.25	0.06
			$s_1^2 = 114$			$s_2^2 = 26.5$		$s_3^2 = 14.6$		$s_4^2 = 3.7$		$s_5^2 = 0.09$	
			$\sigma_1^2 = 57$			$\sigma_1^2 = 13.25$		$\sigma_3^2 = 7.3$		$\sigma_4^2 = 1.85$		$\sigma_5^2 = 0.045$	

This procedure is continued by further varying α and k until we find their best values, that is, those values that minimize the sum of the squares. Many well-known searching techniques are available to obtain the minimum value σ_m^2 .¹¹ Figure 5-10 shows a hypothetical plot of the sum of the squares as a function of the parameters α and k :

$$\sigma^2 = f(k, \alpha) \quad (5-35)$$

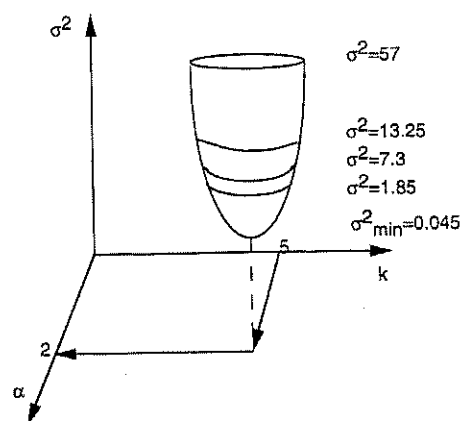


Figure 5-10 Minimum sum of squares.

In searching to find the parameter values that give the minimum of the sum of squares σ^2 , one can use a number of optimization techniques or software packages. The procedure begins by guessing parameter values [e.g., Table 5-2 ($\alpha = 1$, $k = 1 \text{ s}^{-1}$)] and then calculating r_c and then σ^2 for these values (see, e.g., the sixth column in Table 5-2). Next a few sets of parameters are chosen around the initial guess, and σ^2 is calculated for these sets as well. The search technique looks for the smallest value of σ^2 in the vicinity of the initial guess and then proceeds along a trajectory in the direction of decreasing σ^2 to choose different parameter values and determine the corresponding σ^2 . The trajectory is continually adjusted so as always to proceed in the direction of decreasing σ^2 until the minimum value of σ^2 is reached. A schematic of this procedure is shown in Figure 5-11, where the parameter values at the minimum are $\alpha = 2$ and $k = 5 \text{ s}^{-1}$. If the equations are highly nonlinear, the initial guess is extremely important. In some cases it is useful to try different initial guesses of the parameter to make sure that the software program converges on

Vary the initial guesses of parameters to make sure you find the true minimum

¹¹(a) B. Carnahan and J. O. Wilkes, *Digital Computing and Numerical Methods* (New York: Wiley, 1973), p. 405. (b) D. J. Wilde and C. S. Beightler, *Foundations of Optimization* (Upper Saddle River, N.J.: Prentice Hall, 1967). (c) D. Miller and M. Frenklach, *Int. J. Chem. Kinet.*, 15, 677 (1983).

$$k = 5 \text{ s}^{-1} \\ \alpha = 2$$

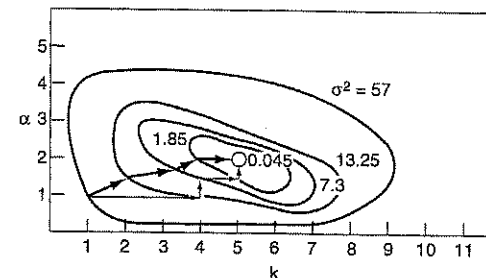


Figure 5-11 Trajectory to find the best values of k and α .

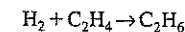
the same minimum for the different initial guesses. The dark lines and heavy arrows represent a computer trajectory, and the light lines and arrows represent the hand calculations shown in Table 5-2.

A number of software packages are available to carry out the procedure to determine the best estimates of the parameter values and the corresponding confidence limits. All one has to do is to type the experimental values in the computer, specify the model, enter the initial guesses of the parameters, and then push the computer button, and the best estimates of the parameter values along with 95% confidence limits appear. If the confidence limits for a given parameter are larger than the parameter itself, the parameter is probably not significant and should be dropped from the model. After the appropriate model parameters are eliminated, the software is run again to determine the best fit with the new model equation.

Model Discrimination. One can also determine which model or equation best fits the experimental data by comparing the sums of the squares for each model and then choosing the equation with a smaller sum of squares and/or carrying out an F-test. Alternatively, we can compare the residual plots for each model. These plots show the error associated with each data point and one looks to see if the error is randomly distributed or if there is a trend in the error. When the error is randomly distributed, this is an additional indication that the correct rate law has been chosen. To illustrate these principles, let's look at the following example.

Example 5-6 Hydrogenation of Ethylene to Ethane

The hydrogenation (H) of ethylene (E) to form ethane (EA),



is carried out over a cobalt molybdenum catalyst [*Collect. Czech. Chem. Commun.*, 51, 2760 (1988)]. Carry out a nonlinear least-squares analysis on the data given in Table E5-6.1, and determine which rate law best describes the data.

TABLE E5-6.1. DIFFERENTIAL REACTOR DATA

Run Number	Reaction Rate (mol/kg cat. · s)	P_E (atm)	P_{EA} (atm)	P_H (atm)
1	1.04	1	1	1
2	3.13	1	1	3
3	5.21	1	1	5
4	3.82	3	1	3
5	4.19	5	1	3
6	2.391	0.5	1	3
7	3.867	0.5	0.5	5
8	2.199	0.5	3	3
9	0.75	0.5	5	1

Determine which of the following rate laws best describes the data.

$$(a) -r_A = \frac{kP_E P_H}{1 + K_A P_{EA} + K_E P_E} \quad (c) -r_A = \frac{kP_E P_H}{(1 + K_E P_E)^2}$$

$$(b) -r_A = \frac{kP_E P_H}{1 + K_E P_E} \quad (d) -r_A = kP_E^a P_H^b$$

Solution

POLYMATH was chosen as the software package to solve this problem. The data in Table E5-6.1 were typed into the system. The following copies of the computer screens illustrate the procedure.

1. First we enter the data in Table E5-6.1 into the POLYMATH table shown in Table E5-6.2. After entering the data and pressing shift F7, the following solution options appear on the screen:

SOLUTION OPTIONS	
1. Do linear regression.	L. Linear regression without free parameter.
p. Fit a polynomial.	P. Polynomial passing through origin.
s. Fit a cubic spline.	R. Do nonlinear regression.
↑ ↓ or F8 for problem options	

Next we type R and choose a model to fit the data.

2. Specify the model and determine the model parameters and σ^2 . The first model we choose is model (a).

$$-r_A = \frac{kP_E P_H}{1 + K_A P_{EA} + K_E P_E} \quad (E5-6.1)$$

Next we enter the model Equation (E5-6.1) and initial estimates of the parameter values.

SOLUTION OPTIONS	
Enter the model equation (↑ ↓ to cancel):	
R=k*Pe*Ph2/(1+Ke*Pe+Ka*Pea)	

- Procedure**
- Enter data
 - Enter model
 - Make initial estimates of parameters
 - Run regression
 - Examine parameters and variance
 - Observe error distribution
 - Choose model

TABLE E5-6.2. ANALYZING RATE DATA

Name	Pe	Ph2	Pea	ra			
1	1	1	1	1.04			
2	1	3	1	3.13			
3	1	5	1	5.21			
4	3	3	1	3.82			
5	5	3	1	4.19			
6	0.5	3	1	2.391			
7	0.5	5	0.5	3.867			
8	0.5	3	3	2.199			
9	0.5	1	5	0.75			
10							
11							
12							
13							
14							
15							
16							
17							
18							

PROBLEM OPTIONS

↑ ↓ to edit current box. ↑ ↓, →, ←, PgUp, PgDn, Home, End to move pointer.
 ↑ ↓ for row/column options.
 ↑ F7 to fit a curve or do regression.
 ↑ F8 for file and library options.
 ↑ to change title.
 F6 for helpful information.
 F7 to print problem.

Details for using regression software

After entering the estimates the following screen appears:

Nonlinear Regression of Rate Data

Nonlinear regression model equation:

$$ra=k*Pe*Ph2/(1+Ke*Pe+Ka*Pea)$$

Initial estimates:

$$k = 1$$

$$Ke = 1$$

$$Ka = 0.01$$

REGRESSION OPTIONS	
1. Change the model equation.	
2. Change the initial guesses.	
↑ F7 to solve.	
F8 for the problem options.	

after which we press shift ↑F7 to solve the problem and the following screen appears:

Param.	Converged Value	0.95 conf. interval	lower limit	upper limit
k	3.34788	0.391055	2.95682	3.73893
K _e	2.21108	0.318885	1.89219	2.52996
K _a	0.0428414	0.0713596	-0.0285181	0.114201

Model: $r_A = k P_E P_H^2 / (1 + K_E P_E + K_A P_A)$

k = 3.34788
K_e = 2.21108

K_a = 0.0428414

6 positive residuals, 3 negative residuals. Sum of squares = 0.0296167

$$-r_A = \frac{3.35 P_E P_H}{1 + 0.043 P_{EA} + 2.2 P_E} \quad (\text{E5-6.2})$$

3. Next we examine the estimated parameters. We see from this last output that the mean value of K_A is 0.043 atm^{-1} , with the 95% confidence limits being ± 0.0712 . The 95% confidence limit on K_A means essentially that if the experiment were performed 100 times, the calculated value of K_A would fall between -0.028 and 0.114 ninety-five out of the hundred times, that is,

$$K_A = 0.043 \pm 0.071 \quad (\text{E5-6.3})$$

For this model, the value of the 95% confidence interval is greater than the value of the parameter itself! Consequently, we are going to set the parameter value K_A equal to zero. When we set K_A equal to zero this yields the second model, model (b).

$$-r_A = \frac{k P_E P_H}{1 + K_E P_E} \quad (\text{E5-6.4})$$

4. Determine the model parameters and σ^2 for the second model. When this model is entered, the following results are obtained:

$$-r_A = \frac{3.19 P_E P_H}{1 + 2.1 P_E} \quad (\text{E5-6.5})$$

The value of the minimum sum of squares is $\sigma_B^2 = 0.042$.

Param.	Converged Value	0.95 conf. interval	lower limit	upper limit
k	3.18678	0.288026	2.89876	3.47481
K _e	2.10133	0.263925	1.83741	2.36526

Model: $r_A = k P_E P_H^2 / (1 + K_E P_E)$

k = 3.18678
K_e = 2.10133

5 positive residuals, 4 negative residuals. Sum of squares = 0.0423735

5. Determine the parameters and σ^2 for a third model. We now proceed to model (c),

$$-r_A = \frac{k P_E P_H}{(1 + K_E P_E)^2} \quad (\text{E5-6.6})$$

for which the following results are obtained:

Param.	Converged Value	0.95 conf. interval	lower limit	upper limit
k	2.00878	0.266198	1.74258	2.27498
K _e	0.361667	0.0623113	0.299356	0.423979

Model: $r_A = k P_E P_H^2 / (1 + K_E P_E)^2$

k = 2.00878

K_e = 0.361667

5 positive residuals, 4 negative residuals. Sum of squares = 0.436122

$$-r_A = \frac{2 P_E P_H}{(1 + 0.36 P_E)^2} \quad (\text{E5-6.7})$$

Comparing the sums of squares for models (b) and (c), we see that model (b) gives the smaller sum ($\sigma_B^2 = 0.042$ versus $\sigma_C^2 = 0.436$) by an order of magnitude, that is,

$$\frac{\sigma_C^2}{\sigma_B^2} = \frac{0.436}{0.042} = 10.38$$

Therefore, we eliminate model (c) from consideration.¹²

6. Determine the parameters and σ^2 for a power law model. Finally, we enter in model (d).

$$-r_A = k P_E^a P_H^b \quad (\text{E5-6.8})$$

The following results were obtained.

Param.	Converged Value	0.95 conf. interval	lower limit	upper limit
k	0.894025	0.256901	0.637124	1.15093
a	0.258441	0.0708914	0.18755	0.329332
b	1.06155	0.209307	0.852246	1.27086

Model: $r_A = k P_E^a P_H^b$

k = 0.894025

b = 1.06155

a = 0.258441

5 positive residuals, 4 negative residuals. Sum of squares = 0.297223

One observes the error ($r_{im} - r_{ic}$) is indeed randomly distributed, indicating the model chosen is most likely the correct one.

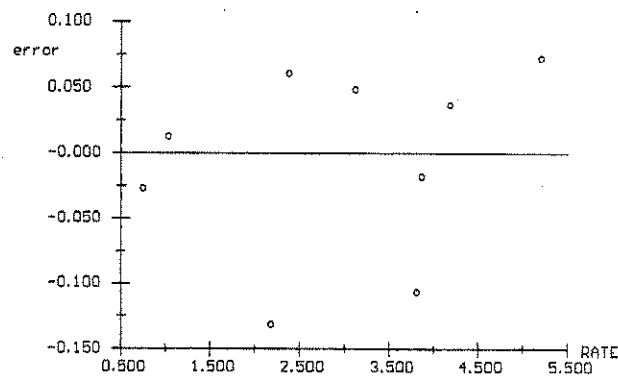
$$-r_A = 0.89 P_E^{0.26} P_H^{1.06} \quad (\text{E5-6.9})$$

7. Choose the best model. Again, the sum of squares for model (d) is significantly higher than in model (b) ($\sigma_B = 0.042$ versus $\sigma_D = 0.297$). Hence, we choose model (b) as our choice to fit the data. For cases when the sums of squares are relatively close together, we can use the F-test to discriminate between models to learn if one model is statistically better than another.¹³

¹²See G. F. Froment and K. B. Bischoff, *Chemical Reaction Analysis and Design*, 2nd ed. (New York: Wiley, (1990), p. 96.

¹³Ibid.

Note that the error is not a function of rate and appears to be randomly distributed



error = RATE - (k*Pe*PH2/(1+Ke*Pe))
k = 3.18678
Ke = 2.10133

Figure E5-6.1 Error as a function of calculated rate.



However, there is a caution! One cannot simply carry out a regression and then pick the model with the lowest value of the sums of squares. If this were the case, we would have chosen model (a) with $\sigma^2 = 0.03$. One must consider the physical realism of the parameters. In model (a) the 95% confidence interval was greater than the parameter itself, thereby yielding negative values of the parameter, K_A , which is physically impossible.

We can also use nonlinear regression to determine the rate law parameters from concentration-time data obtained in batch experiments. We recall that the combined rate law-stoichiometry-mole balance for a constant-volume batch reactor is

$$\frac{dC_A}{dt} = -kC_A^\alpha \quad (5-6)$$

We now integrate Equation (5-6) to give

$$C_{A0}^{1-\alpha} - C_A^{1-\alpha} = (1-\alpha)kt$$

Rearranging to obtain the concentration as a function of time, we obtain

$$C_A = [C_{A0}^{1-\alpha} - (1-\alpha)kt]^{1/(1-\alpha)} \quad (5-36)$$

Now we could use POLYMATH or MATLAB to find the values of α and k that would minimize the sum of squares of the differences between the measured and calculated concentrations. That is, for N data points,

$$s^2 = \sum_{i=1}^N (C_{A_{mi}} - C_{A_{ci}})^2 = \sum_{i=1}^N (C_{A_{mi}} - [C_{A0}^{1-\alpha} - (1-\alpha)kt_i]^{1/(1-\alpha)})^2 \quad (5-37)$$

we want the values of α and k that will make s^2 a minimum.

If POLYMATH is used, one should use the absolute value for C_{Ac} , which is the term in brackets in Equation (5-33), that is,

$$s^2 = \sum_{i=1}^N [C_{A_{mi}} - (\text{abs}[C_{A0}^{1-\alpha} - (1-\alpha)kt_i])^{1/(1-\alpha)}]^2 \quad (5-38)$$

Another way to solve for the parameter values is to use time rather than concentrations:

$$t_c = \frac{C_{A0}^{1-\alpha} - C_A^{1-\alpha}}{k(1-\alpha)} \quad (5-39)$$

That is, we find the values of k and α that minimize

$$s^2 = \sum_{i=1}^N (t_{mi} - t_{ci})^2 = \sum_{i=1}^N \left[t_{mi} - \frac{C_{A0}^{1-\alpha} - C_{Ai}^{1-\alpha}}{k(1-\alpha)} \right]^2 \quad (5-40)$$

Discussion of weighted least squares as applied to a first-order reaction is provided on the CD-ROM.

5.5.3 Weighted Least-Squares Analysis

Both the linear and nonlinear least-squares analyses presented above assume that the variance is constant throughout the range of the measured variables. If this is not the case, a weighted least-squares analysis must be used to obtain better estimates of the rate law parameters. If the error in measurement is at a fixed level, the relative error in the dependent variable will increase as the independent variable increases (decreases). For example, in a first-order decay reaction ($C_A = C_{A0}e^{-kt}$), if the error in concentration measurement is $0.01C_{A0}$, the relative error in the concentration measurement $[0.01C_{A0}/C_A(t)]$ will increase with time. When this error condition occurs, the sum to be minimized for N measurements is

$$\sigma^2 = \sum_{i=1}^N W_i [y_i(\text{exptl}) - y_i(\text{calc})]^2$$

where W_i is a weighting factor.

For parameter estimation involving exponents, it has been shown that a weighted least-squares analysis is usually necessary.¹⁴ Further discussion on weighted least squares as applied to a first-order reaction is given on the CD-ROM.

¹⁴A. C. Norris, *Computational Chemistry: An Introduction to Numerical Solution* (New York: Wiley, 1981), and D. M. Himmelblau, *Process Analysis by Statistical Methods* (New York: Wiley, 1970), p. 195.

5.6 Experimental Planning

Four to six weeks in the lab can save you an hour in the library.

G. C. Quarderer, Dow Chemical Co.

So far, this chapter has presented various methods of analyzing rate data. It is just as important to know in which circumstances to use each method as it is to know the mechanics of these methods. In this section we discuss a heuristic to plan experiments to generate the data necessary for reactor design. However, only a thumbnail sketch is presented; for a more thorough discussion the reader is referred to the books and articles by Box and Hunter.¹⁵

Figure 5-12 provides a road map to help plan an experimental program. A discussion of each of the items in Figure 5-12 appears on the CD-ROM along with an example of an experimental design to study the kinetics of an enzymatic reaction that depends on pH, temperature (T), and concentration (C). Figure 5-13 shows the placement of high and low settings of each of these variables.

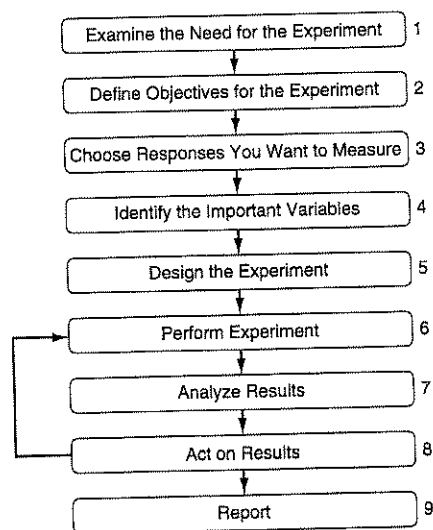


Figure 5-12 Flowchart for experimental projects.

Enzyme degradation is believed to occur at temperatures above 50°C and pH values above 9.5 and below 3.0. The rate of reaction is negligible at temperatures below 6°C. For an urea concentration below 0.001 M , the reaction

¹⁵G. E. P. Box, W. G. Hunter, and J. S. Hunter, *Statistics for Experimenters: An Introduction to Design, Data Analysis, and Model Building* (New York: Wiley, 1978).

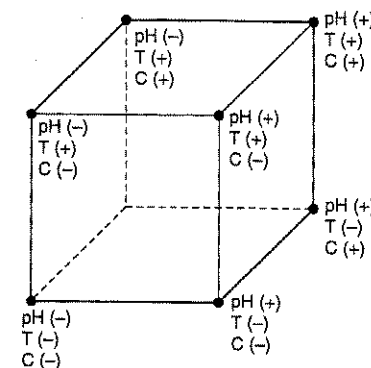


Figure 5-13 Placement (high/low) of controlled variables.

will not proceed at a measurable rate and the rate appears to be independent of concentration above 0.1 M . Consequently, the following high/low values of the parameters were chosen:

A	(-)	pH 4	(+)	pH 8
B	(-)	10°C	(+)	40°C
C	(-)	0.005 M	(+)	0.1 M

This example is discussed further on the CD-ROM.

5.7 Evaluation of Laboratory Reactors

The successful design of industrial reactors lies primarily with the *reliability of the experimentally determined parameters used in the scale-up*. Consequently, it is imperative to design equipment and experiments that will generate accurate and meaningful data. Unfortunately, there is usually no single comprehensive laboratory reactor that could be used for all types of reactions and catalysts. In this section we discuss the various types of reactors that can be chosen to obtain the kinetic parameters for a specific reaction system. We closely follow the excellent strategy presented in the article by V. W. Weekman of Mobil Oil.¹⁶ The criteria used to evaluate various types of laboratory reactors are listed in Table 5-3.

TABLE 5-3. CRITERIA USED TO EVALUATE LABORATORY REACTORS

1. Ease of sampling and product analysis
2. Degree of isothermality
3. Effectiveness of contact between catalyst and reactant
4. Handling of catalyst decay
5. Reactor cost and ease of construction

¹⁶V. W. Weekman, *AIChE J.*, 20, 833 (1974).

Each type of reactor is examined with respect to these criteria and given a rating of good (G), fair (F), or poor (P). What follows is a brief description of each of the laboratory reactors. The reasons for rating each reactor for each of the criteria are given in the CD-ROM.

5.7.1 Integral (Fixed-Bed) Reactor

One advantage of the integral reactor is its ease of construction (see Figure 5-14). On the other hand, while channeling or bypassing of some of the catalyst by the reactant stream may not be as fatal to data interpretation in the case of this reactor as in that of the differential reactor, it may still be a problem.

Easy to construct

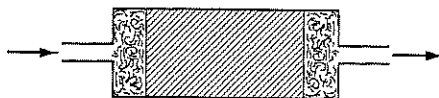


Figure 5-14 Integral reactor.

5.7.2 Stirred Batch Reactor

In the stirred batch reactor the catalyst is dispersed as a slurry, as shown in Figure 5-15. Although there will be better contacting between the catalyst and the fluid in this reactor than either the differential or integral reactors, there is a sampling problem in this reactor.

Good-fluid solid contact

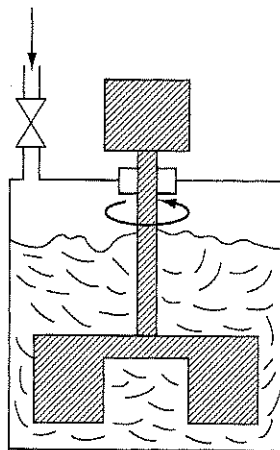


Figure 5-15 Stirred batch reactor. [From V. Weekman, *AIChE J.* 20, 833, (1974) with permission of the AIChE. Copyright © 1974 AIChE. All rights reserved.]

5.7.3 Stirred Contained Solids Reactor (SCSR)

Although there are a number of designs for contained solids reactors, all are essentially equivalent in terms of performance. A typical design is shown in Figure 5-16

Minimizes external mass transfer resistance

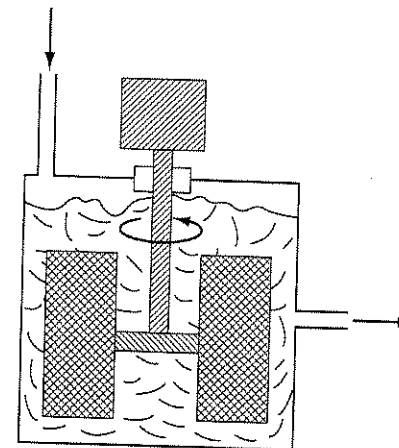


Figure 5-16 Stirred contained solids reactor. [From V. Weekman, *AIChE J.* 20, 833, (1974) with permission of the AIChE. Copyright © 1974 AIChE. All rights reserved.]

5.7.4 Continuous-Stirred Tank Reactor (CSTR)

The CSTR reactor (Figure 5-17) is used when there is significant catalyst decay. Fresh catalyst is fed to the reactor along with the fluid feed, and the cat-

One of the best reactors for isothermal operation

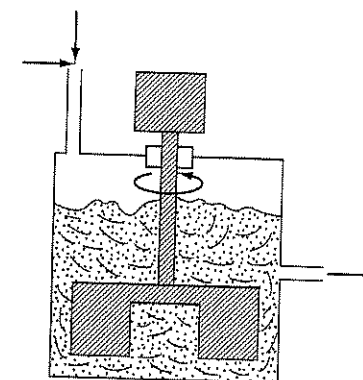


Figure 5-17 [From V. Weekman, *AIChE J.* 20, 833, (1974) with permission of the AIChE. Copyright © 1974 AIChE. All rights reserved.]

alyst leaves the reactor in the product stream at the same rate at which it is fed, to offset catalyst decay with time.

5.7.5 Straight-Through Transport Reactor

Commercially, the transport reactor (Figure 5-18) is used widely in the production of gasoline from heavier petroleum fractions. In addition, it has found use in the drying of grains. In this reactor, either an inert gas or the reactant itself transports the catalyst through the reactor.

Best for catalyst decay

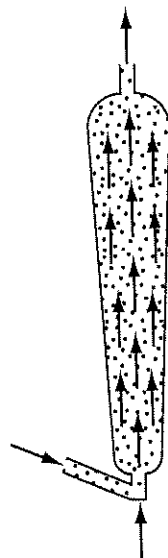


Figure 5-18 Straight-through transport reactor. [From V. Weekman, *AIChE J.* 20, 833, (1974) with permission of the AIChE. Copyright © 1974 AIChE. All rights reserved.]

5.7.6 Recirculating Transport Reactor

By recirculating the gas and catalyst through the transport reactor (Figure 5-19), one can achieve a well-mixed condition provided that the recirculation rate is large with respect to the feed rate.

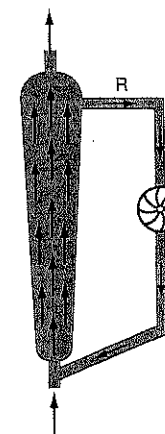


Figure 5-19 Recirculating transport reactor. [From V. Weekman, *AIChE J.* 20, 833, (1974) with permission of the AIChE. Copyright © 1974 AIChE. All rights reserved.]

5.7.7 Summary of Reactor Ratings

The ratings of the various reactors are summarized in Table 5-4. From this table one notes that the CSTR and recirculating transport reactor appear to be the best choices because they are satisfactory in every category except for construction. However, if the catalyst under study does not decay, the stirred batch and contained solids reactors appear to be the best choices. If the system is not limited by internal diffusion in the catalyst pellet, larger pellets could be used and the stirred-contained solids is the best choice. If the catalyst is nondecaying and heat effects are negligible, the fixed-bed (integral) reactor would be the top choice, owing to its ease of construction and operation. However, in practice, usually *more than one* reactor type is used in determining the reaction rate law parameters.

TABLE 5-4. SUMMARY OF REACTOR RATINGS: GAS-LIQUID, POWDERED CATALYST, DECAYING CATALYST SYSTEM^a

Reactor Type	Sampling and Analysis	Isothermality	Fluid-Solid Contact	Decaying Catalyst	Ease of Construction
Differential	P-F	F-G	F	P	G
Fixed bed	G	P-F	F	P	G
Stirred batch	F	G	G	P	G
Stirred-contained solids	G	G	F-G	P	F-G
Continuous-stirred tank	F	G	F-G	F-G	P-F
Straight-through transport	F-G	P-F	F-G	G	F-G
Recirculating transport	F-G	G	G	F-G	P-F
Pulse	G	F-G	P	F-G	G

^aG, good; F, fair; P, poor.

SUMMARY

1. Differential method for constant-volume systems

$$-\frac{dC_A}{dt} = kC_A^\alpha \quad (\text{S5-1})$$

- Plot $\Delta C_A/\Delta t$ as a function of t .
- Determine dC_A/dt from this plot.
- Taking the ln of both sides of (S5-1) gives

$$\ln\left(-\frac{dC_A}{dt}\right) = \ln k + \alpha \ln C_A \quad (\text{S5-2})$$

Plot $\ln(-dC_A/dt)$ versus $\ln C_A$. The slope will be the reaction order α . We could also use finite-difference formulas or software packages to evaluate $-dC_A/dt$ as a function of time and concentration.

2. Integral method

- Guess the reaction order and integrate the mole balance equation.
 - Calculate the resulting function of concentration for the data and plot it as a function of time. If the resulting plot is linear, you have probably guessed the correct reaction order.
 - If the plot is not linear, guess another order and repeat the procedure.
3. *Method of initial rates:* In this method of analysis of rate data, the slope of a plot of $\ln(-r_{A0})$ versus $\ln C_{A0}$ will be the reaction order.
4. *Modeling the differential reactor:* The rate of reaction is calculated from the equation

$$-r'_A = \frac{F_{A0}X}{W} = \frac{F_P}{W} = \frac{v_0(C_{A0} - C_{Ae})}{W} = \frac{C_P v_0}{W} \quad (\text{S5-3})$$

In calculating the reaction order, α ,

$$-r'_A = kC_A^\alpha$$

the concentration of A is evaluated either at the entrance conditions or at a mean value between C_{A0} and C_{Ae} .

5. Least-squares analysis

- Linear least-squares:* Linearize the rate law and solve the resulting algebraic equations [i.e., Equations (5-26) through (5-28)] for the reaction rate law parameters.

$$Y = a_0 + a_1 X_1 + a_2 X_2 \quad (\text{S5-4})$$

- Nonlinear least-squares:* Search for the parameters of the rate law that will minimize the sum of the squares of the difference between the measured rate of reaction and the rate of reaction calculated

from the parameter values chosen. For N experimental runs and K parameters to be determined,

$$\sigma_{\min}^2 = \sum_{i=1}^N \frac{[r_i(\text{measured}) - r_i(\text{calculated})]^2}{N - K} \quad (\text{S5-5})$$

6. Experimental planning (from CD-ROM)

- Why?
- Within what limits?
- Are you choosing the correct parameters?
- Standards!
- Can you do it again?
- Be careful: you can lie with statistics.
- We don't believe an experiment until it's proved by theory.
- Milk your data for all its information.
- Tell the world!

Review Figure 5-13.

QUESTIONS AND PROBLEMS

The subscript to each of the problem numbers indicates the level of difficulty: A, least difficult; D, most difficult.

A = ● B = ■ C = ◆ D = ♦♦

In each of the questions and problems below, rather than just drawing a box around your answer, write a sentence or two describing how you solved the problem, the assumptions you made, the reasonableness of your answer, what you learned, and any other facts that you want to include. You may wish to refer to W. Strunk and E. B. White, *The Elements of Style* (New York: Macmillan, 1979), and Joseph M. Williams, *Style: Ten Lessons in Clarity & Grace* (Glenview, Ill.: Scott, Foresman, 1989) to enhance the quality of your sentences.



- P5-1A (a) Compare Table 5-4 on laboratory reactors with a similar table on page 269 of Bisio and Kabel (see Supplementary Reading, listing 4). What are the similarities and differences?
- (b) Develop an experimental plan that would determine the mechanism and rate law of an unknown reaction.
- (c) Create an original problem based on Chapter 5 material.
- (d) Design an experiment for the undergraduate laboratory that demonstrates the principles of chemical reaction engineering and will cost less than \$500 in purchased parts to build. (1998 AIChE National Student Chapter Competition) Rules are provided on the CD-ROM.
- (e) Plant a number of seeds in different pots (corn works well). The plant and soil of each pot will be subjected to different conditions. Measure the height of the plant as a function of time and fertilizer concentration. Other variables might include lighting, pH, and room temperature.

P5-2_A What if...

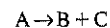
- (a) the reaction you were asked to apply the differential method of analysis to determine the rate law for a reaction that is reversible at the temperature of interest?
- (b) the gas-phase reaction you are studying in your laboratory were extremely toxic. What precautions would you take?

P5-3_A The irreversible isomerization

was carried out in a *batch reactor* and the following concentration–time data were obtained:

t (min)	0	3	5	8	10	12	15	17.5
C_A (mol/dm ³)	4.0	2.89	2.25	1.45	1.0	0.65	0.25	0.07

- (a) Determine the reaction order, α , and the specific reaction rate, k_A .
- (b) If you were to repeat this experiment to determine the kinetics, what would you do differently? Would you run at a higher, lower, or the same temperature? Take different data points? Explain.
- (c) It is believed that the technician made a dilution error in the concentration measured at 17.5 min. What do you think? How do your answers compare using regression (POLYMATH or other software) with those obtained by graphical methods? (Ans.: (a) $k = 0.2$ (mol/dm³)^{1/2}/min)

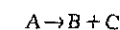
P5-4_A The liquid-phase irreversible reaction

is carried out in a CSTR. To learn the rate law the volumetric flow rate, v_0 , (hence $\tau = V/v_0$) is varied and the effluent concentrations of species A recorded as a function of the space time τ . Pure A enters the reactor at a concentration of 2 mol/dm³. Steady-state conditions exist when the measurements are recorded.

Run	1	2	3	4	5
τ (min)	15	38	100	300	1200
C_A (mol/dm ³)	1.5	1.25	1.0	0.75	0.5

- (a) Determine the reaction order and specific reaction rate.
- (b) If you were to repeat this experiment to determine the kinetics, what would you do differently? Would you run at a higher, lower, or the same temperature? If you were to take more data, where would you place the measurements (e.g., τ)?
- (c) It is believed that the technician may have made a dilution factor-of-10 error in one of the concentration measurements. What do you think? How do your answers compare using regression (POLYMATH or other software) compare with those obtained by graphical methods?

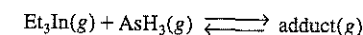
Note: All measurements were taken at steady-state conditions.

P5-5_B The reaction

was carried out in a constant-volume batch reactor where the following concentration measurements were recorded as a function of time.

t (min)	0	5	9	15	22	30	40	60
C_A (mol/dm ³)	2	1.6	1.35	1.1	0.87	0.70	0.53	0.35

- (a) Use nonlinear least squares (i.e., regression) and one other method to determine the reaction order α and the specific reaction rate.
- (b) If you were to take more data, where would you place the points? Why? GaInAs films are important materials in fiber optic communication and in high-speed microelectronic devices. A preliminary reaction between triethylindium and arisine is carried out to form an intermediate, which is then used in the deposition to form GaInAs. The reaction is



The data in Table P5-6 were obtained in a *plug-flow reactor* [JECS, 135(6), 1530 (1988)]. Total pressure (including inerts) = 152.0 torr.

TABLE P5-6

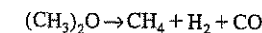
Distance Down Reactor (cm)	Et ₃ In (torr) for AsH ₃ (torr inlet) of:		
	1.5	0.25	3.0
0	0.129	0.129	0.129
1.5	0.075	0.095	0.045
2.5	0.05	0.085	0.022
4.0	0.03	0.08	0.01
6.5	0.018	0.042	0.01
9.0	0.016	0.04	0.01

P5-7_B Find a rate law consistent with the experimental data.

The following data were reported [C. N. Hinshelwood and P. J. Ackey, *Proc. R. Soc. (Lond.)*, A115, 215 (1927)] for a gas-phase constant-volume decomposition of dimethyl ether at 504°C in a *batch reactor*. Initially, only (CH₃)₂O was present.

Time (s)	390	777	1195	3155	∞
Total Pressure (mmHg)	408	488	562	799	931

- (a) Why do you think the total pressure measurement at $t = 0$ is missing? Can you estimate it?
- (b) Assuming that the reaction



is irreversible and goes to completion, determine the reaction order and specific reaction rate k .

- (c) What experimental conditions would you suggest if you were to obtain more data?
- (d) How would the data and your answers change if the reaction were run at a higher or lower temperature?

P5-8_B In order to study the photochemical decay of aqueous bromine in bright sunlight, a small quantity of liquid bromine was dissolved in water contained in a glass battery jar and placed in direct sunlight. The following data were obtained:

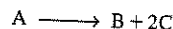
Time (min)	10	20	30	40	50	60
ppm Br ₂	2.45	1.74	1.23	0.88	0.62	0.44

temperature = 25°C

- (a) Determine whether the reaction rate is zero, first, or second order in bromine, and calculate the reaction rate constant in units of your choice.
- (b) Assuming identical exposure conditions, calculate the required hourly rate of injection of bromine (in pounds) into a sunlit body of water, 25,000 gal in volume, in order to maintain a sterilizing level of bromine of 1.0 ppm. (Ans.: 0.43 lb/h)
- (c) What experimental conditions would you suggest if you were to obtain more data?

(Note: ppm = parts of bromine per million parts of brominated water by weight. In dilute aqueous solutions, 1 ppm = 1 milligram per liter.) (California Professional Engineers Exam)

P5-9_C The gas-phase decomposition



is carried out in a *constant-volume batch reactor*. Runs 1 through 5 were carried out at 100°C while run 6 was carried out at 110°C.

- (a) From the data in Table P5-9, determine the reaction order and specific reaction rate.
- (b) What is the activation energy for this reaction?

TABLE P5-9 RAW DATA

Run	Initial Concentration, C_{A0} (g mol/L)	Half-Life, $t_{1/2}$ (min)
1	0.0250	4.1
2	0.0133	7.7
3	0.010	9.8
4	0.05	1.96
5	0.075	1.3
6	0.025	2.0

P5-10_C The reactions of ozone were studied in the presence of alkenes [R. Atkinson et al., *Int. J. Chem. Kinet.*, 15(8), 721 (1983)]. The data in Table P5-10 are for one of the alkenes studied, *cis*-2-butene. The reaction was carried out isothermally at 297 K. Determine the rate law and the values of the rate law parameters.

TABLE P5-10 RAW DATA

Run	Ozone Rate (mol/s · dm ³ × 10 ⁷)	Ozone Concentration (mol/dm ³)	Butene Concentration (mol/dm ³)
1	1.5	0.01	10 ⁻¹²
2	3.2	0.02	10 ⁻¹¹
3	3.5	0.015	10 ⁻¹⁰
4	5.0	0.005	10 ⁻⁹
5	8.8	0.001	10 ⁻⁸
6	4.7	0.018	10 ⁻⁹

(Hint: Ozone also decomposes by collision with the wall)

P5-11_A Tests were run on a small experimental reactor used for decomposing nitrogen oxides in an automobile exhaust stream. In one series of tests, a nitrogen stream containing various concentrations of NO₂ was fed to a reactor and the kinetic data obtained are shown in Figure P5-11. Each point represents one complete run. The reactor operates essentially as an *isothermal backmix reactor (CSTR)*. What can you deduce about the apparent order of the reaction over the temperature range studied?

The plot gives the fractional decomposition of NO₂ fed versus the ratio of reactor volume V (in cm³) to the NO₂ feed rate, $F_{NO_2,0}$ (g mol/h), at different feed concentrations of NO₂ (in parts per million by weight).

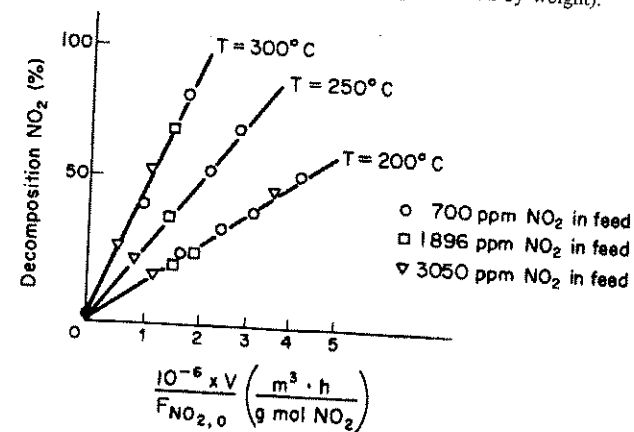


Figure P5-11

P5-12_B Microelectronic devices are formed by first forming SiO₂ on a silicon wafer by chemical vapor deposition (Figure P5-12; cf. Problem P3-25). This procedure is followed by coating the SiO₂ with a polymer called a photoresist. The pattern of the electronic circuit is then placed on the polymer and the sample is irradiated with ultraviolet light. If the polymer is a positive photoresist, the sections that were irradiated will dissolve in the appropriate solvent and those sections not irradiated will protect the SiO₂ from further treatment. The wafer is then exposed to strong acids, such as HF, which etch (i.e., dissolve) the

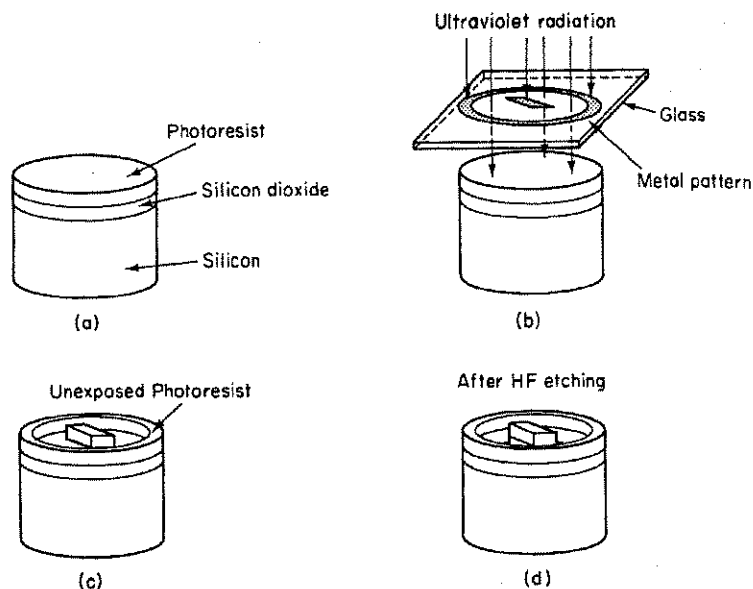
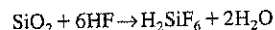


Figure P5-12

exposed SiO_2 . It is extremely important to know the kinetics of the reaction so that the proper depth of the channel can be achieved. The dissolution reaction is

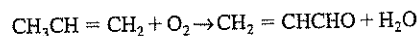


From the following initial rate data, determine the rate law.

Etching Rate (nm/min)	60	200	600	1000	1400
HF (wt %)	8	20	33	40	48

A total of 1000 thin wafer chips are to be placed in 0.5 dm^3 of 20% HF. If a spiral channel $10 \mu\text{m}$ wide and 10 m in length were to be etched to a depth of $50 \mu\text{m}$ on both sides of each wafer, how long should the chips be left in the solution? Assume that the solution is well mixed. (Ans.: 330 min)

P5-13_b The oxidation of propene (P) to acrolein (A) was carried out over a Mo-Pr-Bi catalyst [Ind. Eng. Chem. Res., 26, 1419 (1987)].



It has been proposed to correlate the data using the power law model for the rate law [cf. Equation (5-2)].

$$r_{\text{acrolein}} = k P_P^\alpha P_{\text{O}_2}^\beta$$

The reaction was carried out in a differential reactor with 0.5 g of catalyst at 623 K . From the data below, determine the reaction orders with respect to propene (α) and oxygen (β) and the specific reaction rate, k .

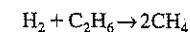
F_A (mmol/h)	0.21	0.48	0.09	0.39	0.6	0.14	1.44
P_P (atm)	0.1	0.2	0.05	0.3	0.4	0.05	0.5
P_{O_2} (atm)	0.1	0.2	0.05	0.01	0.02	0.4	0.5

where F_A = exiting molar flow rate of acrolein, mmol/h

P_P = entering partial pressure of propene, atm

P_{O_2} = entering partial pressure of oxygen, atm

P5-14_b The ethane hydrogenolysis over a commercial nickel catalyst was studied in a stirred contained solids reactor.



(a) Determine the rate law parameters from the data in Table P5-14. There are four spinning baskets, each with 10 g of catalyst. Only hydrogen and ethane are fed to the reactor at 300°C . (Ans.: $k = 0.48 \text{ (mol} \cdot \text{atm/kg} \cdot \text{h)}$)

TABLE P5-14 RAW DATA

Total Molar Feed Rate to Reactor (g mol/h)	Partial Pressure (atm) in Feed		Mole Fraction CH_4 in Exit Stream
	Ethane, $P_{\text{A}0}$	Hydrogen, $P_{\text{B}0}$	
1.7	0.5	0.5	0.05
1.2	0.5	0.5	0.07
0.6	0.5	0.5	0.16
0.3	0.4	0.6	0.16
0.75	0.6	0.6	0.10
2.75	0.6	0.4	0.06

(b) What experimental conditions would you suggest if you were to obtain more data?

P5-15_c The thermal decomposition of isopropyl isocyanate was studied in a differential packed-bed reactor. From the data in Table P5-15, determine the reaction rate law parameters.

TABLE P5-15 RAW DATA

Run	Rate (mol/s · dm ³)	Concentration (mol/dm ³)	Temperature (K)
1	4.9×10^{-4}	0.2	700
2	1.1×10^{-4}	0.02	750
3	2.4×10^{-3}	0.05	800
4	2.2×10^{-2}	0.08	850
5	1.18×10^{-1}	0.1	900
6	1.82×10^{-2}	0.06	950

P5-16_B Mixtures of hydrocarbons (e.g., petroleum feedstocks) that undergo cracking reactions or hydrodemethylation can sometimes be *lumped* as just one reactant or as two or more reactants. In many cases it is difficult to distinguish lumping as a single reactant with second-order kinetics from lumping as two reactants each with first-order kinetics [*Ind. Eng. Chem. Process Des. Dev.*, 19, 197 (1980)]. To distinguish between these two cases, the initial reactant concentration must be varied in more than one run and conversions greater than 92% should be sought in taking the data.

From the *batch reactor* data below, determine whether first-order kinetics for lumping as two reactants A and B or second-order kinetics for lumping one reactant D best describes the system. Experimental conditions are such that one can neglect volume change.

Mechanism I	Mechanism II
Two species	One species
A $\xrightarrow{k_A}$ products	D $\xrightarrow{k_D}$ products
B $\xrightarrow{k_B}$ products	
$C(t) = C_A(t) + C_B(t)$	$C(t) = C_D(t)$

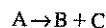
Only the total concentration of the lumped reactant, $C(t)$, can be monitored as a function of time. For two-parameter lumping, estimates of the initial concentrations are $C_{A0} = 0.008 \text{ kmol/m}^3$ and $C_{B0} = 0.006 \text{ kmol/m}^3$.

t (s)	0	10	20	30	40	60	80
Concentration (kmol/m ³)	0.014	0.0115	0.0097	0.0084	0.0074	0.0060	0.0051

Where would you place additional data points?

- P5-17_D** Prepare a detailed experimental plan to learn the rate law for
- The hydrogenation of cyclopentane on a Pt/Al₂O₃ catalyst.
 - The liquid-phase production of methyl bromide from an aqueous solution of methyl amine and bromine cyanide.
 - The acid-catalyzed production of ethylene glycol from an aqueous solution of ethylene oxide.

P5-18_B The irreversible liquid-phase reaction



is carried out in a batch reactor. The following data were collected during the course of the reaction:

t (min)	0.0	2.0	4.0	6.0
C_A (mol/dm ³)	2.00	1.31	0.95	0.73

Determine the order of reaction and the specific reaction rate using methods to differentiate your data.

- Numerical technique—differentiation formulas. (Use Δ 's to represent these points on any graphs you make.)

Graphical technique—equal area differentiation. (Use O's to represent these points on any graphs you make.)

- Differentiating a polynomial. (use x for these points)
- Determine the reaction order.
- Assume a rate law of the form

$$-r_A = kC_A^\alpha$$

Integrate the equation for the combined mole balance and rate law and then use nonlinear least-squares analysis to determine α and k .

P5-19_C (d) Where would you place additional data points? The dehydrogenation of methylcyclohexane (M) to produce toluene (T) was carried out over a 0.3% Pt/Al₂O₃ catalyst in a differential catalytic reactor. The reaction is carried out in the presence of hydrogen (H₂) to avoid coking [*J. Phys. Chem.*, 64, 1559 (1960)].

- Determine the model parameters for each of the following rate laws.

$$(1) -r'_M = kP_M^\alpha P_{H_2}^\beta \quad (3) -r'_M = \frac{kP_M P_{H_2}}{(1 + K_M P_M)^2}$$

$$(2) -r'_M = \frac{kP_M}{1 + K_M P_M} \quad (4) -r'_M = \frac{kP_M P_{H_2}}{1 + K_M P_M + K_{H_2} P_{H_2}}$$

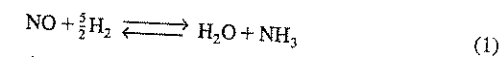
Use the data in Table P5-19.

TABLE P5-19 DEHYDROGENATION OF METHYLCYCLOHEXANE

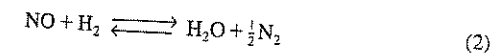
P_{H_2} (atm)	P_M (atm)	r'_T $\left(\frac{\text{mol toluene}}{\text{s} \cdot \text{kg cat.}}\right)$
1	1	1.2
1.5	1	1.25
0.5	1	1.30
0.5	0.5	1.1
1	0.25	0.92
0.5	0.1	0.64
3	3	1.27
1	4	1.28
3	2	1.25
4	1	1.30
0.5	0.25	0.94
2	0.05	0.41

- Which rate law best describes the data? (*Hint:* We will learn in Chapter 10 that neither K_{H_2} or K_M can take on negative values.)
- Where would you place additional data points?

P5-20_C In the production of ammonia



the following side reaction occurs:



Ayen and Peters [*Ind. Eng. Chem. Process Des. Dev.*, 1, 204 (1962)] studied catalytic reaction of nitric oxide with Girdler G-50 catalyst in a differential reactor at atmospheric pressure. Table P5-20 shows the reaction rate of the side reaction as a function of P_{H_2} and P_{NO} at a temperature of 375°C.

TABLE P5-20 FORMATION OF AMMONIA

P_{H_2} (atm)	P_{NO} (atm)	Reaction Rate
		$r_{H_2O} \times 10^3$ (g mol/min · g cat.) $T = 375^\circ\text{C}$, $W = 2.39$ g
0.00922	0.0500	1.60
0.0136	0.0500	2.56
0.0197	0.0500	3.27
0.0280	0.0500	3.64
0.0291	0.0500	3.48
0.0389	0.0500	4.46
0.0485	0.0500	4.75
0.0500	0.00918	1.47
0.0500	0.0184	2.48
0.0500	0.0298	3.45
0.0500	0.0378	4.06
0.0500	0.0491	4.75

The following rate laws for side reaction (2), based on various catalytic mechanisms, were suggested:

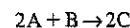
$$r_{H_2O} = \frac{kK_{NO}P_{NO}P_{H_2}}{1 + K_{NO}P_{NO} + K_{H_2}P_{H_2}} \quad (3)$$

$$r_{H_2O} = \frac{kK_{H_2}K_{NO}P_{NO}}{1 + K_{NO}P_{NO} + K_{H_2}P_{H_2}} \quad (4)$$

$$r_{H_2O} = \frac{k_1K_{H_2}K_{NO}P_{NO}P_{H_2}}{(1 + K_{NO}P_{NO} + K_{H_2}P_{H_2})^2} \quad (5)$$

Find the parameter values of the different rate laws and determine which rate law best represents the experimental data.

P5-21_B For the reaction



the experimental rate data listed in Table P5-21 have been obtained.

- Is this reaction elementary? Defend your conclusion with supporting reasoning and/or analysis.
- Why is the sequence specified the way it is?
- Where would you place additional experiments?

TABLE P5-21 RAW DATA

Run	r_c (mol/dm ³ · s)	P_A (atm)	P_B (atm)
1	0.6	1	0.5
4	1.2	1	1
9	4.2	1	4
8	8.1	1	10
7	9.6	2	2
3	11.0	3	1
5	53	2	30
6	59.3	5	2
10	200	5	10
2	250	5	15

JOURNAL CRITIQUE PROBLEMS

- P5C-1** A packed-bed reactor was used to study the reduction of nitric oxide with ethylene on a copper-silica catalyst [*Ind. Eng. Chem. Process Des. Dev.*, 9, 455 (1970)]. Develop the integral design equation in terms of the conversion at various initial pressures and temperatures. Is there a significant discrepancy between the experimental results shown in Figures 2 and 3 in the article and the calculated results based on the proposed rate law? If so, what is the possible source of this deviation?
- P5C-2** Equation (3) in the article [*J. Chem. Technol. Biotechnol.*, 31, 273 (1981)] is the rate of reaction and is incorporated into design equation (2). Rederive the design equation in terms of conversion. Determine the rate dependence on H_2 based on this new equation. How does the order obtained compare with that found by the authors?
- P5C-3** In "The kinetics of the oxidation of hydrogen chloride over molten salt catalysts," *Chem. Eng. Sci.*, 23, 981 (1968), use Figure 2 in the article to determine the initial rate of HCl oxidation for the various oxygen concentrations. Include these data in Figure 3 together with the other data. Is it possible to explain the curvature in the line at small partial pressures of chlorine (the square root of the partial pressure of Cl_2)?
- P5C-4** See "Kinetics of catalytic esterification of terephthalic acid with methanol vapour," *Chem. Eng. Sci.*, 28, 337 (1973). When one observes the data points in Figure 2 of this paper for large times, it is noted that the last data point always falls significantly off the straight-line interpretation. Is it possible to reanalyze these data to determine if the chosen reaction order is indeed correct? Substituting your new rate law into equation (3), derive a new form of equation (10) in the paper relating time and particle radius.
- P5C-5** The kinetics of vapor-phase ammoxidation of 3-methylpyridine over a promoted V_2O_5 - Al_2O_3 catalyst was reported in *Chem. Eng. Sci.*, 35, 1425 (1980). Suggest a mechanism and rate-limiting step consistent with each of the two mechanisms proposed. In each case how would you plot the data to extract the rate law parameters? Which mechanism is supported by the data?
- P5C-6** The selective oxidation of toluene and methanol over vanadium pentoxide-supported alkali metal sulfate catalysts was studied recently [*AIChE J.*, 27(1), 41

(1981)]. Examine the experimental technique used (equipment, variables, etc.) in light of the mechanism proposed. Comment on the shortcomings of the analysis and compare with another study of this system presented in *AIChE J.*, 28(5), 855 (1982).



CD-ROM MATERIAL

- **Learning Resources**

1. *Summary Notes for Lectures 9 and 10*
3. *Interactive Computer Modules*
 - A. Ecology
4. *Solved Problems*
 - A. CDP5-B_B Oxygenating Blood
 - B. Example CD5-1 Integral Method of Analysis of Pressure-Time Data

- **Living Example Problems**

1. *Example 5-6 Hydrogenation of Ethylene to Ethane*

- **Professional Reference Shelf**

1. *Weighted Least Squares Analysis*
2. *Experimental Planning*
3. *Evaluation of Laboratory Reactors*

- **FAQ [Frequently Asked Questions]—In Updates/FAQ icon section**

- **Additional Homework Problems**

- CDP5-A_B** The reaction of penicillin G with NH_2OH is carried out in a batch reactor. A colorimeter was used to measure the absorbency as a function of time. [1st Ed. P5-10]
- CDP5-B_B** The kinetics of the deoxygenating of hemoglobin in the blood was studied with the aid of a tubular reactor. [1st Ed. P5-3]
- CDP5-C_C** The kinetics of the formation of an important propellant ingredient, triaminoguanidine, were studied in a batch reactor where the ammonia concentration was measured as a function of time. [2nd Ed. P5-6]
- CDP5-D_B** The half-life of one of the pollutants, NO, in autoexhaust is required. [1st Ed. P5-11]
- CDP5-E_B** The kinetics of a gas-phase reaction $\text{A}_2 \rightarrow 2\text{A}$ were studied in a constant-pressure batch reactor in which the volume was measured as a function of time. [1st Ed. P5-6]

SUPPLEMENTARY READING

1. A wide variety of techniques for measuring the concentrations of the reacting species may be found in

ROBINSON, J. W., *Undergraduate Instrumental Analysis*, 5th ed. New York: Marcel Dekker, 1995.

SKOOG, D. A., *Principles of Instrumental Analysis*, 3rd ed. Philadelphia: Holt, Rinehart and Winston, 1985.

2. A discussion on the methods of interpretation of batch reaction data can be found in

CRYNES, B. L., and H. S. FOGLER, eds., *AIChE Modular Instruction Series E: Kinetics*, Vol. 2. New York: American Institute of Chemical Engineers, 1981, pp. 51-74.

3. The interpretation of data obtained from flow reactors is also discussed in

CHURCHILL, S. W., *The Interpretation and Use of Rate Data*. New York: McGraw-Hill, 1974.

SMITH, J. M., *Chemical Engineering Kinetics*, 3rd ed. New York: McGraw-Hill, 1981, Chap. 4.

4. The design of laboratory catalytic reactors for obtaining rate data is presented in

RASE, H. F., *Chemical Reactor Design for Process Plants*, Vol. 1. New York: Wiley, 1983, Chap. 5.

Most of these types of reactors are also discussed in

ANDERSON, R. B., ed. *Experimental Methods in Catalytic Research*. New York: Academic Press, 1968.

5. Model building and current statistical methods applied to interpretation of rate data are presented in

FROMENT, G. F., and K. B. BISCHOFF, *Chemical Reactor Analysis and Design*. New York: Wiley, 1979.

KITTRELL, J. R., in *Advances in Chemical Engineering*, Vol. 8, T. B. Draw et al., eds. New York: Academic Press, 1970, pp. 97-183.

JOHANSEN, S., *Functional Relations, Random Coefficients, and Nonlinear Regression with Application to Kinetic Data*, New York: Springer-Verlag, 1984.

MARKERT, B. A., *Instrumental Element and Multi-Element Analysis of Plant Samples: Methods and Applications*, New York: Wiley, 1996.

6. The sequential design of experiments and parameter estimation is covered in

BOX, G. E. P., W. G. HUNTER, and J. S. HUNTER, *Statistics for Experimenters: An Introduction to Design, Data Analysis, and Model Building*. New York: Wiley, 1978.

GRAHAM, R. J., and F. D. STEVENSON, *Ind. Eng. Chem. Process Des. Dev.*, 11, 160 (1972).

Multiple Reactions 6

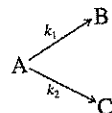
The breakfast of champions is not cereal, it's your opposition.

Nick Seitz

Seldom is the reaction of interest the *only one* that occurs in a chemical reactor. Typically, multiple reactions will occur, some desired and some undesired. One of the key factors in the economic success of a chemical plant is the minimization of undesired side reactions that occur along with the desired reaction.

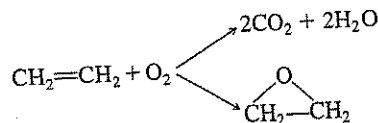
In this chapter we discuss reactor selection and general mole balances for multiple reactions. There are three basic types of multiple reactions: series, parallel, and independent. In *parallel reactions* (also called *competing reactions*) the reactant is consumed by two different reaction pathways to form different products:

Parallel reactions



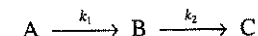
An example of an industrially significant parallel reaction is the oxidation of ethylene to ethylene oxide while avoiding complete combustion to carbon dioxide and water.

Serious chemistry

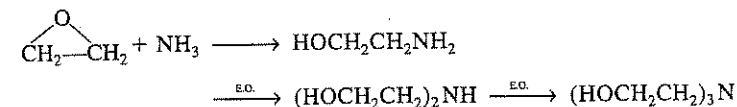


In *series reactions*, also called *consecutive reactions*, the reactant forms an intermediate product, which reacts further to form another product:

Series reactions



An example of a series reaction involving ethylene oxide (E.O.) is its reaction with ammonia to form mono-, di-, and triethanolamine:



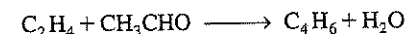
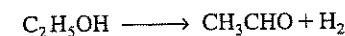
In recent years the shift has been toward the production of diethanolamine as the *desired* product rather than triethanolamine.

Multiple reactions involve a combination of both series and parallel reactions, such as



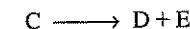
An example of a combination of parallel and series reactions is the formation of butadiene from ethanol:

Simultaneous series and parallel reactions



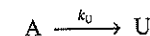
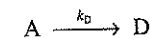
Independent reactions are of the type

Independent reactions



and occur in feed stocks containing many reactants. The cracking of crude oil to form gasoline is an example where independent reactions take place.

The first part of this chapter will be concerned primarily with parallel reactions. Of particular interest are reactants that are consumed in the formation of a *desired product*, D, and the formation of an *undesired product*, U, in a competing or side reaction. In the reaction sequence



we want to minimize the formation of U and maximize the formation of D, because the greater the amount of undesired product formed, the greater the cost of separating the undesired product U from the desired product D (Figure 6-1).

In a highly efficient and costly reactor scheme in which very little of undesired product U is formed in the reactor, the cost of the separation process could be quite low. On the other hand, even if a reactor scheme is inexpensive and inefficient, resulting in the formation of substantial amounts of U, the cost

The economic incentive

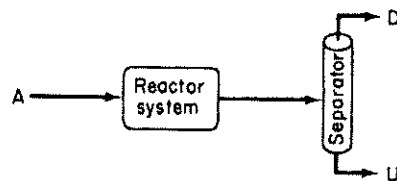


Figure 6-1 Reaction-separation system producing both desired and undesired products.

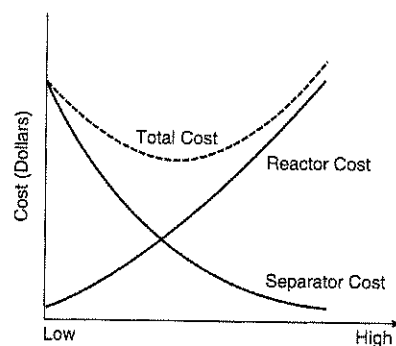


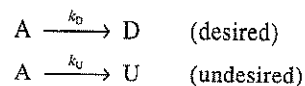
Figure 6-2 Efficiency of a reactor system.

of the separation system could be quite high. Normally, as the cost of a reactor system increases in an attempt to minimize U, the cost of separating species U from D decreases (Figure 6-2).

6.1 Maximizing the Desired Product in Parallel Reactions

In this section we discuss various means of minimizing the undesired product, U, through the selection of reactor type and conditions. We also discuss the development of efficient reactor schemes.

For the competing reactions



the rate laws are

$$r_D = k_D C_A^{\alpha_1} \quad (6-1)$$

$$r_U = k_U C_A^{\alpha_2} \quad (6-2)$$

Rate laws for formation of desired and undesired products

The rate of disappearance of A for this reaction sequence is the sum of the rates of formation of U and D:

$$-r_A = r_D + r_U \quad (6-3)$$

$$-r_A = k_D C_A^{\alpha_1} + k_U C_A^{\alpha_2} \quad (6-4)$$

where α_1 and α_2 are positive constants. We want the rate of formation of D, r_D , to be high with respect to the rate of formation of U, r_U . Taking the ratio of these rates [i.e., Equation (6-1) to Equation (6-2)], we obtain a *rate selectivity parameter*, S , which is to be maximized:

$$S_{DU} = \frac{r_D}{r_U} = \frac{k_D}{k_U} C_A^{\alpha_1 - \alpha_2} \quad (6-5)$$

6.1.1 Maximizing the Rate Selectivity Parameter S for One Reactant

In this section we examine ways to maximize S , which is sometimes referred to as the instantaneous selectivity, for different reaction orders of the desired and undesired products.

Case 1: $\alpha_1 > \alpha_2$ For the case where the reaction order of the desired product is greater than the reaction order of the undesired product, let a be a positive number that is the difference between these reaction orders:

$$\alpha_1 - \alpha_2 = a$$

Then

$$S_{DU} = \frac{r_D}{r_U} = \frac{k_D}{k_U} C_A^a \quad (6-6)$$

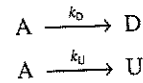
For $\alpha_1 > \alpha_2$, make C_A as large as possible

To make this ratio as large as possible, we want to carry out the reaction in a manner that will keep the concentration of reactant A as high as possible during the reaction. If the reaction is carried out in the gas phase, we should run it without inerts and at high pressures to keep C_A high. If the reaction is in the liquid phase, the use of diluents should be kept to a minimum.¹

A batch or plug-flow reactor should be used in this case, because in these two reactors, the concentration of A starts at a high value and drops progressively during the course of the reaction. In a *perfectly mixed* CSTR, the concentration of reactant within the reactor is always at its lowest value (i.e., that of the outlet concentration) and therefore not be chosen under these circumstances.

¹ For a number of liquid-phase reactions, the proper choice of a solvent can enhance selectivity. See, for example, *Ind. Eng. Chem.*, 62(9), 16 (1970). In gas-phase heterogeneous catalytic reactions, selectivity is an important parameter of any particular catalyst.

Case 2: $\alpha_2 > \alpha_1$ When the reaction order of the undesired product is greater than that of the desired product,



Let $a = \alpha_2 - \alpha_1$, where a is a positive number; then

$$S_{DU} = \frac{r_D}{r_U} = \frac{k_D C_A^{\alpha_1}}{k_U C_A^{\alpha_2}} = \frac{k_D}{k_U C_A^{a}} = \frac{k_D}{k_U C_A^a} \quad (6-7)$$

For the ratio r_D/r_U to be high, the concentration of A should be as low as possible.

This low concentration may be accomplished by diluting the feed with inerts and running the reactor at low concentrations of A. A CSTR should be used, because the concentrations of reactant are maintained at a low level. A recycle reactor in which the product stream acts as a diluent could be used to maintain the entering concentrations of A at a low value.

Because the activation energies of the two reactions in cases 1 and 2 are not known, it cannot be determined whether the reaction should be run at high or low temperatures. The sensitivity of the rate selectivity parameter to temperature can be determined from the ratio of the specific reaction rates,

$$\frac{k_D}{k_U} = \frac{A_D}{A_U} e^{-(E_D - E_U)/RT} \quad (6-8)$$

where A is the frequency factor, E the activation energy, and the subscripts D and U refer to desired and undesired product, respectively.

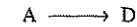
Case 3: $E_D > E_U$ In this case the specific reaction rate of the desired reaction k_D (and therefore the overall rate r_D) increases more rapidly with increasing temperature than does the specific rate of the undesired reaction k_U . Consequently, the reaction system should be operated at the highest possible temperature to maximize S_{DU} .

Case 4: $E_U > E_D$ In this case the reaction should be carried out at a low temperature to maximize S_{DU} , but not so low that the desired reaction does not proceed to any significant extent.

Example 6-1 Minimizing Unwanted Products for a Single Reactant

Reactant A decomposes by three simultaneous reactions to form three products: one that is desired, D, and two that are undesired, Q and U. These gas-phase reactions, together with their corresponding rate laws, are:

Desired product:



$$r_D = \left\{ 0.0012 \exp \left[26,000 \left(\frac{1}{300} - \frac{1}{T} \right) \right] \right\} C_A \quad (E6-1.1)$$

Unwanted product U:



$$r_U = \left\{ 0.0018 \exp \left[25,000 \left(\frac{1}{300} - \frac{1}{T} \right) \right] \right\} C_A^{1.5} \quad (E6-1.2)$$

Unwanted product Q:



$$r_Q = \left\{ 0.00452 \exp \left[5000 \left(\frac{1}{300} - \frac{1}{T} \right) \right] \right\} C_A^{0.5} \quad (E6-1.3)$$

How and under what conditions (e.g., reactor type, pressure, temperature, etc.) should the reactions above be carried out to minimize the concentrations of the unwanted products U and Q?

Solution

Because pre exponential factors are comparable, but the activation energies of reactions (E6-1.1) and (E6-1.2) are much greater than the activation energy of reaction (E6-1.3), the rate of formation of Q will be negligible with respect to the rates of formation of D and U at high temperatures:

$$S_{DQ} = \frac{r_D}{r_Q} \approx \text{very large} \quad (E6-1.4)$$

Now we need only to consider the relative rates of formation of D and U at high temperatures:

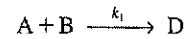
$$S_{DU} = \frac{r_D}{r_U} = \frac{0.66 e^{1000[(1/300) - (1/T)]}}{C_A^{0.5}} \quad (E6-1.5)$$

From Equation (E6-1.5) we observe that the amount of undesired product, U, can be minimized by carrying out the reaction at low concentrations. Therefore, to maximize the conversion of A to D we would want to operate our reactor at high temperatures (to minimize the formation of Q) and at low concentrations of A (to minimize the formation of U). That is, carry out the reaction at

1. High temperatures.
2. Low concentrations of A, which may be accomplished by:
 - a. Adding inerts.
 - b. Using low pressures (if gas phase).
 - c. Using a CSTR or a recycle reactor.

6.1.2 Maximizing the Rate Selectivity Parameter S for Two Reactants

Next consider two simultaneous reactions in which two reactants, A and B, are being consumed to produce a desired product, D, and an unwanted product, U, resulting from a side reaction. The rate laws for the reactions



are

$$r_D = k_1 C_A^{\alpha_1} C_B^{\beta_1} \quad (6-9)$$

$$r_U = k_2 C_A^{\alpha_2} C_B^{\beta_2} \quad (6-10)$$

The rate selectivity parameter

Instantaneous
selectivity

$$S_{DU} = \frac{r_D}{r_U} = \frac{k_1}{k_2} C_A^{\alpha_1 - \alpha_2} C_B^{\beta_1 - \beta_2} \quad (6-11)$$

is to be maximized. Shown in Figure 6-3 are various reactor schemes and conditions that might be used to maximize S_{DU} .

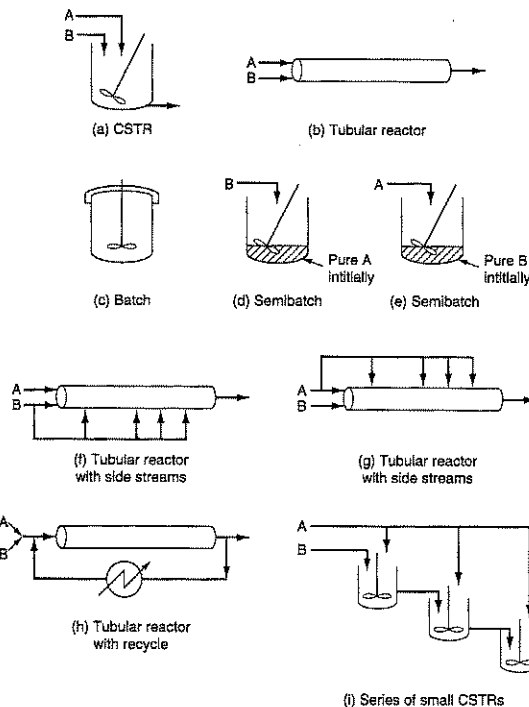
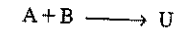
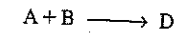


Figure 6-3 Different reactors and schemes for minimizing the unwanted product.

Choose from these or similar schemes to obtain the greatest amount of desired product and least amount of undesired product

Example 6-2 Minimizing Unwanted Products for Two Reactants

For the parallel reactions



consider all possible combinations of reaction orders and select the reaction scheme that will maximize S_{DU} .

Solution

Case I: $\alpha_1 > \alpha_2$, $\beta_1 > \beta_2$. Let $a = \alpha_1 - \alpha_2$ and $b = \beta_1 - \beta_2$, where a and b are positive constants. Using these definitions we can write Equation (6-12) in the form

$$S_{DU} = \frac{r_D}{r_U} = \frac{k_1}{k_2} C_A^a C_B^b \quad (E6-2.1)$$

To maximize the ratio r_D/r_U , maintain the concentrations of both A and B as high as possible. To do this, use:

- A tubular reactor.
- A batch reactor.
- High pressures (if gas phase).

Case II: $\alpha_1 > \alpha_2$, $\beta_1 < \beta_2$. Let $a = \alpha_1 - \alpha_2$ and $b = \beta_2 - \beta_1$, where a and b are positive constants. Using these definitions we can write Equation (E6-2.1) in the form

$$S_{DU} = \frac{r_D}{r_U} = \frac{k_1 C_A^a}{k_2 C_B^b} \quad (E6-2.2)$$

To make S_{DU} as large as possible we want to make the concentration of A high and the concentration of B low. To achieve this result, use:

- A semibatch reactor in which B is fed slowly into a large amount of A (Figure 6-3d).
- A tubular reactor with side streams of B continually fed to the reactor (Figure 6-3f).
- A series of small CSTRs with A fed only to the first reactor and small amounts of B fed to each reactor. In this way B is mostly consumed before the CSTR exit stream flows into the next reactor (Reverse of Figure 6-3i).

Case III: $\alpha_1 < \alpha_2$, $\beta_1 < \beta_2$. Let $a = \alpha_2 - \alpha_1$ and $b = \beta_2 - \beta_1$, where a and b are positive constants. Using these definitions we can write Equation (E6-2.1) in the form

$$S_{DU} = \frac{r_D}{r_U} = \frac{k_1}{k_2 C_A^a C_B^b} \quad (\text{E6-2.3})$$

To make S_{DU} as large as possible, the reaction should be carried out at low concentrations of A and of B. Use:

- A CSTR.
- A tubular reactor in which there is a large recycle ratio.
- A feed diluted with inerts.
- Low pressure (if gas-phase).

Case IV: $\alpha_1 < \alpha_2$, $\beta_1 > \beta_2$. Let $a = \alpha_2 - \alpha_1$ and $b = \beta_1 - \beta_2$, where a and b are positive constants. Using these definitions we can write Equation (E6-2.1) in the form

$$S_{DU} = \frac{r_D}{r_U} = \frac{k_1 C_B^b}{k_2 C_A^a} \quad (\text{E6-2.4})$$

To maximize S_{DU} , run the reaction at high concentrations of B and low concentrations of A. Use:

- A semibatch reactor in which A is slowly fed to a large amount of B.
- A tubular reactor with side streams of A.
- A series of small CSTRs with fresh A fed to each reactor.

Another definition of selectivity used in the current literature, \tilde{S}_{DU} , is given in terms of the flow rates leaving the reactor. S_{DU} is the overall selectivity.

Overall selectivity

$$\tilde{S}_{DU} = \text{selectivity} = \frac{F_D}{F_U} = \frac{\text{exit molar flow rate of desired product}}{\text{exit molar flow rate of undesired product}} \quad (\text{6-12})$$

For a batch reactor, the overall selectivity is given in terms of the number of moles of D and U at the end of the reaction time:

$$\tilde{S}_{DU} = \frac{N_D}{N_U}$$

Two definitions for selectivity and yield are found in the literature

One also finds that the reaction yield, like the selectivity, has two definitions: one based on the ratio of reaction rates and one based on the ratio of molar flow rates. In the first case, the yield at a point can be defined as the

ratio of the reaction rate of a given product to the reaction rate of the key reactant A. This is sometimes referred to as the instantaneous yield.²

Instantaneous yield

Yield based on rates

$$Y_D = \frac{r_D}{-r_A} \quad (\text{6-13})$$

In the case of reaction yield based on molar flow rates, the overall yield, \tilde{Y}_D , is defined as the ratio of moles of product formed at the end of the reaction to the number of moles of the key reactant, A, that have been consumed.

For a batch system:

Overall yield

$$\tilde{Y}_D = \frac{N_D}{N_{A0} - N_A} \quad (\text{6-14})$$

For a flow system:

Overall yield

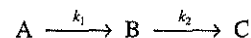
$$\tilde{Y}_D = \frac{F_D}{F_{A0} - F_A} \quad (\text{6-15})$$

As a consequence of the different definitions for selectivity and yield, when reading literature dealing with multiple reactions, check carefully to ascertain the definition intended by the author. From an economic standpoint it is the *overall* selectivities, \tilde{S} , and yields, \tilde{Y} , that are important in determining profits. However, the rate-based selectivities give insights in choosing reactors and reaction schemes that will help maximize the profit. However, many times there is a conflict between selectivity and conversion (yield) because you want to make a lot of your desired product (D) and at the same time minimize the undesired product (U). However, in many instances the greater conversion you achieve, not only do you make more D, you also form more U.

6.2 Maximizing the Desired Product in Series Reactions

In Section 6.1 we saw that the undesired product could be minimized by adjusting the reaction conditions (e.g., concentration) and by choosing the proper reactor. For series of consecutive reactions, the most important variable is time: space-time for a flow reactor and real-time for a batch reactor. To illustrate the importance of the time factor, we consider the sequence

² J. J. Carberry, in *Applied Kinetics and Chemical Reaction Engineering*, R. L. Goring and V. W. Weekman, eds. (Washington, D.C.: American Chemical Society, 1967), p. 89.

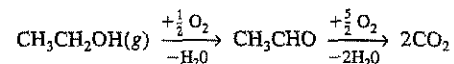


in which species B is the desired product.

If the first reaction is slow and the second reaction is fast, it will be extremely difficult to produce species B. If the first reaction (formation of B) is fast and the reaction to form C is slow, a large yield of B can be achieved. However, if the reaction is allowed to proceed for a long time in a batch reactor, or if the tubular flow reactor is too long, the desired product B will be converted to C. In no other type of reaction is exactness in the calculation of the time needed to carry out the reaction more important than in consecutive reactions.

Example 6-3 Maximizing the Yield of the Intermediate Product

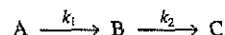
The oxidation of ethanol to form acetaldehyde is carried out on a catalyst of 4 wt % Cu-2 wt % Cr on Al_2O_3 .³ Unfortunately, acetaldehyde is also oxidized on this catalyst to form carbon dioxide. The reaction is carried out in a threefold excess of oxygen and in dilute concentrations (ca. 0.1% ethanol, 1% O_2 , and 98.9% N_2). Consequently, the volume change with the reaction can be neglected. Determine the concentration of acetaldehyde as a function of space-time.



The reactions are irreversible and first-order in ethanol and acetaldehyde, respectively.

Solution

Because O_2 is in excess, we can write the equation above as



1. Mole balance on A:

$$\frac{dF_A}{dW} = r'_A \quad (\text{E6-3.1})$$

a. Rate law:

$$-r'_A = k_1 C_A$$

b. Stoichiometry ($\varepsilon \ll 1$):

$$F_A = C_A v_0$$

c. Combining, we have

$$v_0 \frac{dC_A}{dW} = -k_1 C_A \quad (\text{E6-3.2})$$

Let $\tau' = W/v_0 = \rho_b V/v_0 = \rho_b \tau$, where ρ_b is the bulk density of the catalyst.

³ R. W. McCabe and P. J. Mitchell, *Ind. Eng. Chem. Process Res. Dev.*, 22, 212 (1983).

d. Integrating with $C_A = C_{A0}$ at $W = 0$ gives us

$$C_A = C_{A0} e^{-k_1 \tau'} \quad (\text{E6-3.3})$$

2. Mole balance on B:

$$\frac{dF_B}{dW} = r'_{B_{\text{net}}} \quad (\text{E6-3.4})$$

a. Rate law (net):

$$\begin{aligned} r'_{B_{\text{net}}} &= r'_{B_{\text{rxn1}}} + r'_{B_{\text{rxn2}}} \\ r'_{B_{\text{net}}} &= k_1 C_A - k_2 C_B \end{aligned} \quad (\text{E6-3.5})$$

b. Stoichiometry:

$$F_B = v_0 C_B$$

c. Combining yields

$$v_0 \frac{dC_B}{dW} = k_1 C_A - k_2 C_B \quad (\text{E6-3.6})$$

Substituting for C_A and rearranging, we have

$$\frac{dC_B}{d\tau'} + k_2 C_B = k_1 C_{A0} e^{-k_1 \tau'}$$

d. Using the integrating factor gives us

$$\frac{d(C_B e^{+k_2 \tau'})}{d\tau'} = k_1 C_{A0} e^{(k_2 - k_1) \tau'}$$

At the entrance to the reactor, $W = 0$, $\tau' = W/v_0 = 0$, and $C_B = 0$. Integrating, we get

$$C_B = k_1 C_{A0} \left(\frac{e^{-k_1 \tau'} - e^{-k_2 \tau'}}{k_2 - k_1} \right) \quad (\text{E6-3.7})$$

The concentrations of A, B, and C are shown in Figure E6-3.1.

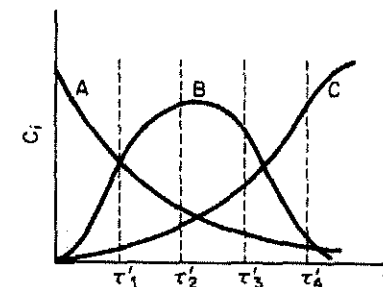


Figure E6-3.1

There is a space time at which B is a maximum

3. **Optimum yield.** The concentration of B goes through a maximum at a point along the reactor. Consequently, to find the optimum reactor length, we need to differentiate Equation (E6-3.7):

$$\frac{dC_B}{d\tau'} = 0 = \frac{k_1 C_{A0}}{k_2 - k_1} (-k_1 e^{-k_1 \tau'} + k_2 e^{-k_2 \tau'}) \quad (\text{E6-3.8})$$

Solving for τ'_{opt} gives

$$\tau'_{\text{opt}} = \frac{1}{k_1 - k_2} \ln \frac{k_1}{k_2} \quad (\text{E6-3.9})$$

$$W_{\text{opt}} = \frac{v_0}{k_1 - k_2} \ln \frac{k_1}{k_2} \quad (\text{E6-3.10})$$

The corresponding conversion of A is

$$\begin{aligned} X_{\text{opt}} &= \frac{C_{A0} - C_A}{C_{A0}} = 1 - e^{-k_1 \tau'} \\ &= 1 - \exp \left[-\ln \left(\frac{k_1}{k_2} \right)^{k_1/(k_1 - k_2)} \right] \\ &= 1 - \left(\frac{k_1}{k_2} \right)^{k_1/(k_2 - k_1)} \end{aligned} \quad (\text{E6-3.11})$$

The yield has been defined as

$$\bar{Y}_A = \frac{\text{moles of acetaldehyde in exit}}{\text{moles of ethanol fed}}$$

and is shown as a function of conversion in Figure E6-3.2.

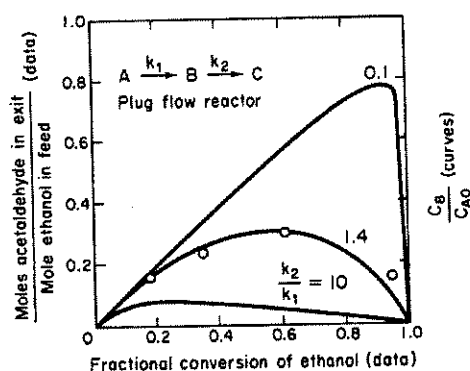


Figure E6-3.2 Yield of acetaldehyde as a function of ethanol conversion. Data were obtained at 518 K. Data points (in order of increasing ethanol conversion) were obtained at space velocities of 26,000, 52,000, 104,000, and 208,000 h⁻¹. The curves were calculated for a first-order series reaction in a plug-flow reactor and show yield of the intermediate species B as a function of the conversion of reactant for various ratios of rate constants k_2 and k_1 . [Reprinted with permission from *Ind. Eng. Chem. Prod. Res. Dev.*, 22, 212 (1983). Copyright © 1983 American Chemical Society.]

Another technique is often used to follow the progress for two reactions in series. The concentrations of A, B and C are plotted as a singular point at different space times (e.g., τ'_1 , τ'_2) on a triangular diagram (see Figure 6-4). The vertices correspond to pure A, B, and C.

For $(k_1/k_2) \gg 1$ a large quantity of B can be obtained

For $(k_1/k_2) \ll 1$ very little B can be obtained

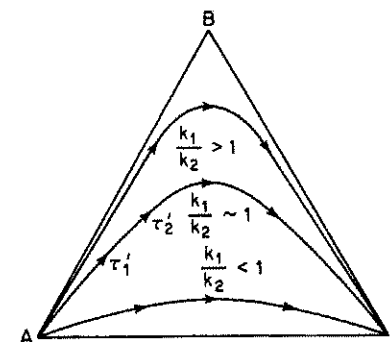


Figure 6-4 Reaction paths for different values of the specific rates.

6.3 Algorithm for Solution to Complex Reactions

6.3.1 Moie Balances

In complex reaction systems consisting of combinations of parallel and series reactions the availability of software packages (ODE solvers) makes it much easier to solve problems using moles N_j or molar flow rates F_j rather than conversion. For liquid systems, concentration may be the preferred variable used in the mole balance equations. The resulting coupled differential equations can be easily solved using an ODE solver. In fact, this section has been developed to take advantage of the vast number of computational techniques now available on mainframe (e.g., Simulso) and personal computers (POLYMATH).

Table 6-1 gives the forms of the mole balances we shall use for complex reactions where r_A and r_B are the net rates of reaction.

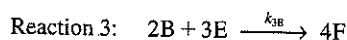
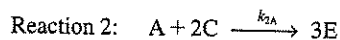
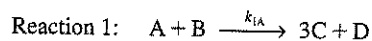
TABLE 6-1. MOLE BALANCES FOR MULTIPLE REACTIONS

Reactor	Gas	Liquid
Batch	$\frac{dN_A}{dt} = r_A V$	$\frac{dC_A}{dt} = r_A$
CSTR	$V = \frac{F_{A0} - F_A}{-r_A}$	$V = v_0 \frac{C_{A0} - C_A}{-r_A}$
PFR/PBR	$\frac{dF_A}{dV} = r_A$	$v_0 \frac{dC_A}{dV} = r_A$
Semibatch	$\frac{dN_A}{dt} = r_A V$	$\frac{dC_A}{dt} = r_A - \frac{v_0 C_A}{V}$
	$\frac{dN_B}{dt} = r_B V + F_{B0}$	$\frac{dC_B}{dt} = r_B + \frac{v_0 [C_{B0} - C_B]}{V}$

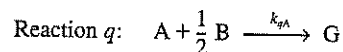
These are the forms of the mole balances we will use for multiple reactions

6.3.2 Net Rates of Reaction

Having written the mole balances, the key point for multiple reactions is to write the **net** rate of formation of each species (e.g., A, B). That is, we have to sum up the rates of formation for each reaction in order to obtain the net rate of formation, e.g. r_A . If q reactions are taking place



⋮



Then the net rates of reaction of A and B are

$$r_A = r_{1A} + r_{2A} + r_{3A} + \cdots + r_{qA} = \sum_{i=1}^q r_{iA}$$

$$r_B = r_{1B} + r_{2B} + r_{3B} + \cdots + r_{qB} = \sum_{i=1}^q r_{iB}$$

Net rates
of reaction

When we sum the rates of the individual reaction for a species, we note that for those reactions in which a species (e.g., A, B) does not appear, the rate is zero. For the first three reactions above, $r_{3A} = 0$, $r_{2B} = 0$, and $r_{2D} = 0$.

To write the reactions above in more compact notation we could let $A_1 = A$, $A_2 = B$, and so on, to arrive at the generic sequence of q reactions shown in Table 6-2. The letter A_j represents a chemical species (e.g., $A_1 = \text{HCl}$, $A_2 = \text{NaOH}$). The first subscript, i , in the stoichiometric coefficient ν_{ij} and in the reaction rate r_{ij} refers to the reaction number while the second subscript, j , refers to the particular species in the reaction. We are now in a position to evaluate the total rate of formation of each species from all reac-

r_{ij}
└ species
└ reaction number

TABLE 6-2

Reaction Number	Reaction Stoichiometry
1	$\nu_{11}A_1 + \nu_{12}A_2 \longrightarrow \nu_{1j}A_j$
2	$\nu_{21}A_1 + \nu_{2j}A_j \longrightarrow \nu_{23}A_3 + \nu_{24}A_4$
⋮	⋮
i	$\nu_{ij}A_j + \nu_{ik}A_k \longrightarrow \nu_{ip}A_p$
⋮	⋮
q	$\nu_{qj}A_j + \nu_{q3}A_3 \longrightarrow \nu_{q5}A_5$

tions. That is, the net rate of reaction for species A_j is the sum of all rates of reaction in which species A_j appears. For q reactions taking place,

$$r_j = \sum_{i=1}^q r_{ij} \quad (6-16)$$

6.3.3 Rate Laws

The rate laws for each of the individual reactions are expressed in terms of concentrations, C_j , of the reacting species. For example, if reaction 2 above (i.e., $A + 2C \rightarrow 3E$) followed an elementary rate law, then the rate of disappearance of A could be

$$-r_{2A} = k_{2A} C_A C_C^2$$

or in terms of the rate of formation of A in reaction 2,

$$r_{2A} = -k_{2A} C_A C_C^2$$

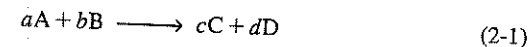
For the general reaction set given in Table 6-2, the rate law for the rate of formation of reactant species A_j in reaction i might depend on the concentration of species A_k and species A_l , for example,

$$r_{ij} = -k_{ij} C_k^2 C_l^3$$

We need to determine the rate law for at least one species in each reaction.

6.3.4 Stoichiometry: Relative Rates of Reaction

The next step is to relate the rate law for a particular reaction and species to other species participating in that reaction. To achieve this relationship we simply recall the generic reaction from Chapters 2 and 3,



and use Equation (2-20) to relate the rates of disappearance of A and B to the rates of formation of C and D:

$$\frac{-r_A}{a} = \frac{-r_B}{b} = \frac{r_C}{c} = \frac{r_D}{d} \quad (2-3)$$

In working with multiple reactions it is usually more advantageous to relate the *rates of formation* of each species to one another. This can be achieved by rewriting (2-20) in the form for reaction i

$$\frac{r_{iA}}{-a_i} = \frac{r_{iB}}{-b_i} = \frac{r_{iC}}{c_i} = \frac{r_{iD}}{d_i} \quad (6-17)$$

$$\left[\text{e.g. for reaction 2: } r_{2C} = \frac{c_2}{-a_2} r_{2A} = \frac{c_2}{a_2} (-r_{2A}) \right]$$

Relative rates of
reaction

Applying Equation (6-17) to reaction 2 above [i.e., $(A + 2C \xrightarrow{k_{2A}} 3E)$ where $r_{2A} = -k_{2A}C_A C_C^2$], the rate of formation of species E, r_{2E} , is

$$r_{2E} = \frac{3}{-1} (r_{2A}) = -3(-k_{2A}C_A C_C^2) = 3k_{2A}C_A C_C^2$$

and the rate of formation of C is

$$r_{2C} = \frac{-2}{-1} r_{2A} = -2k_{2A}C_A C_C^2$$

To relate the relative rates of formation in more compact notation suppose the rate law for the rate of formation of species A_k is given in reaction i as

$$r_{ik} = k_{ik}C_k^2C_2$$

To find the rate of formation of species A_j in reaction i , r_{ij} , we multiply the rate law for species A_k in reaction i by the ratio of stoichiometric coefficients of species A_j , v_{ij} , and species A_k , v_{ik} , in reaction i :

$$\frac{r_{ij}}{v_{ij}} = \frac{r_{ik}}{v_{ik}} \quad (6-18)$$

This relationship only holds for relative rates in the same reaction (i.e., reaction i). When relating relative rates of formation the stoichiometric coefficients, v_{ij} , of reactants are taken as negative and the coefficients of products as positive.

In analyzing the multiple reactions in Table 6-2, we carry out the procedure shown in Table 6-3 (not necessarily in exact order) when the rate law is known for at least one species in each of the individual reactions.

TABLE 6-3. STEPS IN ANALYZING MULTIPLE REACTIONS

1. Number each reaction.
2. Write the mole balances for each species.
3. Determine the rate laws for each species in each reaction.
4. Relate the rate of reaction of each species to the species for which the rate law is given for each reaction.
5. Determine the net rate of formation of each species.
6. Express rate laws as a function of concentration, C_j , for the case of no volume change.
7. Express the rate laws as a function of moles, N_j (batch), or molar flow rates, F_j (flow) when there is volume change with reaction.
8. Combine all of the above and solve the resulting set of coupled differential (PFR, PBR, batch) or algebraic (CSTR) equations.

The multiple-reaction algorithm for isothermal reactions

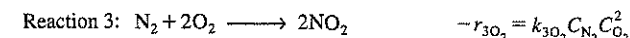
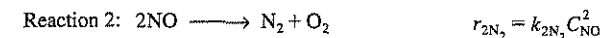
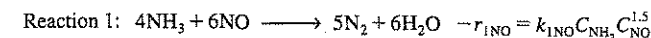
r_{2E}
↑↑ species
↑ reaction
number

Relative rates of reaction in reaction i in compact notation

Example 6-4 Stoichiometry and Rate Laws for Multiple Reactions

Consider the following set of reactions:

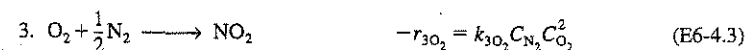
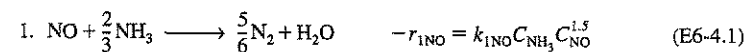
Rate Laws⁴



Write the rate law for each species in each reaction and then write the net rates of formation of NO, O₂, and N₂.

Solution

The rate laws for reactions 1, 2, and 3 are given in terms of species NO, N₂, and O₂, respectively. Consequently, to relate each reacting species in each reaction to its rate law more clearly, we divide each reaction through by the stoichiometric coefficient of the species for which the rate law is given.



The corresponding rate laws are related by:

Recalling Eqn. (6-17)

$$\frac{r_{1A}}{-a_i} = \frac{r_{1B}}{-b_i} = \frac{r_{1C}}{c_i} = \frac{r_{1D}}{d_i}$$

Reaction 1: The rate law w.r.t. NO is

$$-r_{1\text{NO}} = k_{1\text{NO}}C_{\text{NH}_3}C_{\text{NO}}^{1.5}$$

The relative rates are

$$\frac{r_{1\text{NO}}}{(-1)} = \frac{r_{1\text{NH}_3}}{(-2/3)} = \frac{r_{1\text{N}_2}}{(5/6)} = \frac{r_{1\text{H}_2\text{O}}}{(1)}$$

Then the rate of disappearance of NH₃ is

$$-r_{1\text{NH}_3} = \frac{2}{3}(-r_{1\text{NO}}) = \frac{2}{3}k_{1\text{NO}}C_{\text{NH}_3}C_{\text{NO}}^{1.5} \quad (\text{E6-4.4})$$

⁴ From tortusimetry data (11/2/19).

Multiple reaction stoichiometry

$$r_{1N_2} = \frac{5}{6}(-r_{1NO}) = \frac{5}{6}k_{1NO}C_{NH_3}C_{NO}^{1.5} \quad (E6-4.5)$$

$$r_{1H_2O} = -r_{1NO} \quad (E6-4.6)$$

Reaction 2:

$$-r_{2NO} = 2r_{2N_2} = 2k_{2N_2}C_{NO}^2 \quad (E6-4.7)$$

$$r_{2O_2} = r_{2N_2} \quad (E6-4.8)$$

Reaction 3:

$$-r_{3N_2} = \frac{1}{2}(-r_{3O_2}) = \frac{1}{2}k_{3O_2}C_{N_2}C_{O_2}^2 \quad (E6-4.9)$$

$$r_{3NO_2} = -r_{3O_2} \quad (E6-4.10)$$

Next, let us examine the *net* rate of formations. The net rates of formation of NO is:

$$r_{NO} = \sum_{i=1}^3 r_{iNO} = r_{1NO} + r_{2NO} + 0 \quad (E6-4.11)$$

$$r_{NO} = -k_{1NO}C_{NH_3}C_{NO}^{1.5} - 2k_{2N_2}C_{NO}^2 \quad (E6-4.12)$$

Next consider N_2

$$r_{N_2} = \sum_{i=1}^3 r_{iN_2} = r_{1N_2} + r_{2N_2} + r_{3N_2} \quad (E6-4.13)$$

$$r_{N_2} = \frac{5}{6}k_{1NO}C_{NH_3}C_{NO}^{1.5} + k_{2N_2}C_{NO}^2 - \frac{1}{2}k_{3O_2}C_{N_2}C_{O_2}^2 \quad (E6-4.14)$$

Finally O_2

$$r_{O_2} = r_{2O_2} + r_{3O_2} = r_{2N_2} + r_{3O_2} \quad (E6-4.15)$$

$$r_{O_2} = k_{2N_2}C_{NO}^2 - k_{3O_2}C_{N_2}C_{O_2}^2 \quad (E6-4.16)$$

6.3.5 Stoichiometry: Concentrations

Now to express the concentrations in terms of molar flow rates we recall that for liquids

Liquid phase

$$C_j = \frac{F_j}{v_0} \quad (6-19)$$

For ideal gases recall Equation (3-45):

Gas phase

$$C_j = \frac{F_{j0}}{v_0} \left(\frac{F_j}{F_T} \right) \frac{P}{P_0} \frac{T_0}{T} = C_{T0} \left(\frac{F_j}{F_T} \right) \frac{P}{P_0} \frac{T_0}{T} \quad (3-45)$$

where

$$F_T = \sum_{j=1}^n F_j \quad (6-20)$$

and

$$C_{T0} = \frac{P_0}{RT_0} \quad (6-21)$$

For isothermal systems with no pressure drop

Gas phase

$$C_j = C_{T0} \left(\frac{F_j}{F_T} \right) \quad (6-22)$$

and we can express the rates of disappearance of each species as a function of the molar flow rates (F_1, \dots, F_j):

$$r_1 = f n_1 \left(C_{T0} \frac{F_1}{F_T}, C_{T0} \frac{F_2}{F_T}, \dots, C_{T0} \frac{F_j}{F_T} \right) \quad (6-23)$$

$$r_2 = f n_2 \left(C_{T0} \frac{F_1}{F_T}, \dots, C_{T0} \frac{F_j}{F_T} \right) \quad (6-24)$$

where $f n$ represents the functional dependence on concentration of the net rate of formation such as that given in Equation (E6-4.12) for N_2 .

6.3.6 Combining Step

We now insert rate laws written in terms of molar flow rates [e.g., Equation (3-45)] into the mole balances (Table 6-1). After performing this operation for each species we arrive at a coupled set of first-order ordinary differential equations to be solved for the molar flow rates as a function of reactor volume (i.e., distance along the length of the reactor). In liquid-phase reactions, incorporating and solving for total molar flow rate is not necessary at each step along the solution pathway because there is no volume change with reaction.

Combining mole balance, rate laws, and stoichiometry for species 1 through species j in the gas phase and for isothermal operation with no pressure drop gives us

Coupled ODEs

$$\frac{dF_1}{dV} = r_1 = \sum_{i=1}^m r_{i1} = f n_1 \left(C_{T0} \frac{F_1}{F_T}, \dots, C_{T0} \frac{F_j}{F_T} \right) \quad (6-25)$$

⋮

$$\frac{dF_j}{dV} = r_j = \sum_{i=1}^q r_{ij} = f n_j \left(C_{T0} \frac{F_1}{F_T}, \dots, C_{T0} \frac{F_j}{F_T} \right) \quad (6-26)$$

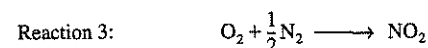
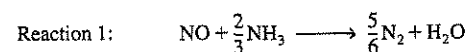
For constant-pressure batch systems we would simply substitute N_i for F_i in the equations above. For constant-volume batch systems we would use concentrations:

$$C_j = N_j / V_0 \quad (6-27)$$

We see that we have j coupled ordinary differential equations that must be solved simultaneously with either a numerical package or by writing an ODE solver. In fact, this procedure has been developed to take advantage of the vast number of computation techniques now available on mainframe (e.g., Simusolv) and personal computers (POLYMATH, Mathematica, MATLAB).

Example 6-5 Combining Mole Balances, Rate Laws, and Stoichiometry for Multiple Reactions

Consider again the reaction in Example 6-4. Write the mole balances on a PFR in terms of molar flow rates for each species.



Solution

For gas-phase reactions, the concentration of species j is

$$C_j = C_{T0} \frac{F_j}{F_T} \frac{P}{P_0} \frac{T_0}{T}$$

For no pressure drop and isothermal operation,

$$C_j = C_{T0} \frac{F_j}{F_T} \quad (\text{E6-5.1})$$

In combining the mole balance, rate laws, and stoichiometry, we will use our results from Example 6-4. The total molar flow rate of all the gases is

$$F_T = F_{\text{NO}} + F_{\text{NH}_3} + F_{\text{N}_2} + F_{\text{H}_2\text{O}} + F_{\text{O}_2} + F_{\text{NO}_2} \quad (\text{E6-5.2})$$

We now rewrite mole balances on each species in the total molar flow rate.

(1) Mole balance on NO:

$$\frac{dF_{\text{NO}}}{dV} = r_{\text{NO}} = -k_{1\text{NO}} C_{\text{NH}_3}^{1.5} C_{\text{NO}} - 2k_{2\text{N}_2} C_{\text{NO}}^2$$

(E6-5.3)

$$\frac{dF_{\text{NO}}}{dV} = -k_{1\text{NO}} C_{T0}^{2.5} \left(\frac{F_{\text{NH}_3}}{F_T} \right) \left(\frac{F_{\text{NO}}}{F_T} \right)^{1.5} - 2k_{2\text{N}_2} C_{T0}^2 \left(\frac{F_{\text{NO}}}{F_T} \right)^2$$

Using the results of Example 6-4

(2) Mole balance on NH_3 :

$$\frac{dF_{\text{NH}_3}}{dV} = r_{\text{NH}_3} = r_{1\text{NH}_3} = \frac{2}{3} r_{1\text{NO}} = -\frac{2}{3} k_{1\text{NO}} C_{\text{NH}_3}^{1.5} C_{\text{NO}}$$

(E6-5.4)

$$\frac{dF_{\text{NH}_3}}{dV} = -\frac{2}{3} k_{1\text{NO}} C_{T0}^{2.5} \left(\frac{F_{\text{NH}_3}}{F_T} \right) \left(\frac{F_{\text{NO}}}{F_T} \right)^{1.5}$$

(3) Mole balance on H_2O :

$$\frac{dF_{\text{H}_2\text{O}}}{dV} = r_{\text{H}_2\text{O}} = r_{1\text{H}_2\text{O}} = -r_{1\text{NO}} = k_{1\text{NO}} C_{\text{NH}_3}^{1.5} C_{\text{NO}}$$

(E6-5.5)

$$\frac{dF_{\text{H}_2\text{O}}}{dV} = k_{1\text{NO}} C_{T0}^{2.5} \left(\frac{F_{\text{NH}_3}}{F_T} \right) \left(\frac{F_{\text{NO}}}{F_T} \right)^{1.5}$$

(4) Mole balance on N_2 :

$$\frac{dF_{\text{N}_2}}{dV} = r_{\text{N}_2} = \frac{5}{6} k_{1\text{NO}} C_{\text{NH}_3}^{1.5} C_{\text{NO}} + k_{2\text{N}_2} C_{\text{NO}}^2 - \frac{1}{2} k_{3\text{O}_2} C_{\text{N}_2} C_{\text{O}_2}^2$$

$$\frac{dF_{\text{N}_2}}{dV} = \frac{5}{6} k_{1\text{NO}} C_{T0}^{2.5} \left(\frac{F_{\text{NH}_3}}{F_T} \right) \left(\frac{F_{\text{NO}}}{F_T} \right)^{1.5} + k_{2\text{N}_2} C_{T0}^2 \left(\frac{F_{\text{NO}}}{F_T} \right)^2 - \frac{1}{2} k_{3\text{O}_2} C_{T0}^3 \left(\frac{F_{\text{N}_2}}{F_T} \right) \left(\frac{F_{\text{O}_2}}{F_T} \right)^2$$

(E6-5.6)

(5) Mole balance on O_2 :

$$\frac{dF_{\text{O}_2}}{dV} = r_{\text{O}_2} = r_{2\text{O}_2} + r_{3\text{O}_2} = r_{2\text{N}_2} + r_{3\text{O}_2}$$

(E6-5.7)

$$\frac{dF_{\text{O}_2}}{dV} = k_{2\text{N}_2} C_{T0}^2 \left(\frac{F_{\text{NO}}}{F_T} \right)^2 - k_{3\text{O}_2} C_{T0}^3 \left(\frac{F_{\text{N}_2}}{F_T} \right) \left(\frac{F_{\text{O}_2}}{F_T} \right)^2$$

(6) Mole balance on NO_2 :

$$\frac{dF_{\text{NO}_2}}{dV} = r_{\text{NO}_2} = r_{3\text{NO}_2} = -r_{3\text{O}_2} = k_{3\text{O}_2} C_{T0}^3 \left(\frac{F_{\text{N}_2}}{F_T} \right) \left(\frac{F_{\text{O}_2}}{F_T} \right)^2$$

(E6-5.8)

The entering molar flow rates, F_{j0} , along with the entering temperature, T_0 , and pressure, P_0 ($C_{T0} = P_0 / RT_0$), are specified as are the specific reaction rates k_{ij} [e.g., $k_{1\text{NO}} = 0.43 \text{ (dm}^3/\text{mol)}^{1.5}/\text{s}$, $k_{2\text{N}_2} = 2.7 \text{ dm}^3/\text{mol} \cdot \text{s}$, etc.]. Consequently, Equations (E6-5.1) through (E6-5.8) can be solved simultaneously with an ODE solver (e.g., POLYMATH, MATLAB).

Summarizing to this point, we show in Table 6-4 the equations for species j and reaction i that are to be combined when we have q reactions and n species.

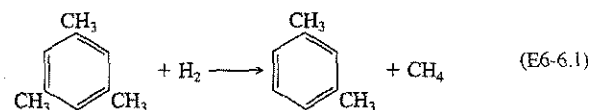
TABLE 6-4. SUMMARY OF RELATIONSHIP FOR MULTIPLE REACTIONS OCCURRING IN A PFR

Mole balance:	$\frac{dF_j}{dV} = r_j$	(6-26)
Rate laws:	$r_{ij} = k_{ij} f_i(C_1, C_j, C_n)$	
Stoichiometry:	$r_j = \sum_{i=1}^q r_{ij}$	(6-16)
	$\frac{r_{iA}}{-a_i} = \frac{r_{iB}}{-b_i} = \frac{r_{iC}}{c_i} = \frac{r_{iD}}{d_i}$	(6-17)
Stoichiometry:	$F_T = \sum_{j=1}^n F_j$	(6-20)
Stoichiometry:		
(gas-phase)	$C_j = C_{T0} \frac{F_j}{F_T} \frac{P}{P_0} \frac{T_0}{T}$	(3-45)
(liquid-phase)	$C_j = \frac{F_j}{v_0}$	(6-19)

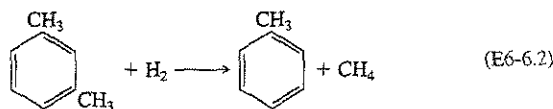
The basic equations

Example 6-6 Hydrodealkylation of Mesitylene in a PFR

The production of *m*-xylene by the hydrodealkylation of mesitylene over a Houdry Detrol catalyst⁵ involves the following reactions:



m-Xylene can also undergo hydrodealkylation to form toluene:



A significant economic incentive

The second reaction is undesirable, because *m*-xylene sells for a higher price than toluene (65 cents/lb vs. 11.4 cents/lb).⁶ Thus we see that there is a significant incentive to maximize the production of *m*-xylene.

⁵ Ind. Eng. Chem. Process Des. Dev., 4, 92 (1965); 5, 146 (1966).

⁶ September 1996 prices, from Chemical Market Reporter (Schnell Publishing Co.), 252, 29 (July 7, 1997). Also see <http://www.chemweek.com/>

The hydrodealkylation of mesitylene is to be carried out isothermally at 1500°R and 35 atm in a packed-bed reactor in which the feed is 66.7 mol% hydrogen and 33.3 mol% mesitylene. The volumetric feed rate is 476 ft³/h and the reactor volume (i.e., $V = W/\rho_b$) is 238 ft³.

The rate laws for reactions 1 and 2 are, respectively,

$$-r_{1M} = k_1 C_M C_H^{0.5} \quad (\text{E6-6.3})$$

$$r_{2T} = k_2 C_X C_H^{0.5} \quad (\text{E6-6.4})$$

where the subscripts are: M = mesitylene, X = *m*-xylene, T = toluene, Me = methane, and H = hydrogen (H₂).

At 1500°R the specific reaction rates are:

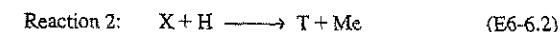
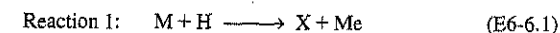
$$\text{Reaction 1: } k_1 = 55.20 \text{ (ft}^3/\text{lb mol)}^{0.5}/\text{h}$$

$$\text{Reaction 2: } k_2 = 30.20 \text{ (ft}^3/\text{lb mol)}^{0.5}/\text{h}$$

The bulk density of the catalyst has been included in the specific reaction rate (i.e., $k_1 = k'_1 \rho_b$).

Plot the concentrations of hydrogen, mesitylene, and xylene as a function of space-time. Calculate the space-time where the production of xylene is a maximum (i.e., τ_{opt}).

Solution



1. Mole balances:

$$\text{Hydrogen: } \frac{dF_H}{dV} = r_{1H} + r_{2H} \quad (\text{E6-6.5})$$

$$\text{Mesitylene: } \frac{dF_M}{dV} = r_{1M} \quad (\text{E6-6.6})$$

$$\text{Xylene: } \frac{dF_X}{dV} = r_{1X} + r_{2X} \quad (\text{E6-6.7})$$

$$\text{Toluene: } \frac{dF_T}{dV} = r_{2T} \quad (\text{E6-6.8})$$

$$\text{Methane: } \frac{dF_{\text{Me}}}{dV} = r_{1\text{Me}} + r_{2\text{Me}} \quad (\text{E6-6.9})$$

2. Rate laws:

$$\text{Reaction 1: } -r_{1H} = k_1 C_H^{1/2} C_M \quad (\text{E6-6.3})$$

$$\text{Reaction 2: } r_{2T} = k_2 C_H^{1/2} C_X \quad (\text{E6-6.4})$$

3. Stoichiometry (no volume change with reaction, $v = v_0$)

a. Reaction rates:

$$\text{Reaction 1: } -r_{1H} = -r_{1M} = r_{1X} = r_{1Me} \quad (\text{E6-6.10})$$

$$\text{Reaction 2: } -r_{2H} = -r_{2X} = r_{2T} = r_{2Me} \quad (\text{E6-6.11})$$

b. Flow rates:

$$F_H = v_0 C_H \quad (\text{E6-6.12})$$

$$F_M = v_0 C_M \quad (\text{E6-6.13})$$

$$F_X = v_0 C_X \quad (\text{E6-6.14})$$

$$F_{Me} = v_0 C_{Me} = F_{H0} - F_H = v_0 (C_{H0} - C_H) \quad (\text{E6-6.15})$$

$$F_T = F_{M0} - F_M - F_X = v_0 (C_{M0} - C_M - C_X) \quad (\text{E6-6.16})$$

4. Combining and substituting in terms of the space-time yields

$$\tau = \frac{V}{v_0}$$

If we know C_M , C_H , and C_X , then C_{Me} and C_T can be calculated from the reaction stoichiometry. Consequently, we need only to solve the following three equations:

$$\frac{dC_H}{d\tau} = -k_1 C_H^{1/2} C_M - k_2 C_X C_H^{1/2} \quad (\text{E6-6.17})$$

$$\frac{dC_M}{d\tau} = -k_1 C_H^{1/2} C_M \quad (\text{E6-6.18})$$

$$\frac{dC_X}{d\tau} = k_1 C_H^{1/2} C_M - k_2 C_X C_H^{1/2} \quad (\text{E6-6.19})$$

5. Parameter evaluation:

$$C_{H0} = \frac{y_{H0} P_0}{RT} = \frac{(0.667)(35)}{(0.73)(1500)} = 0.021 \text{ lb mol/ft}^3$$

$$C_{M0} = \frac{1}{2} C_{H0} = 0.0105 \text{ lb mol/ft}^3$$

$$C_{X0} = 0$$

$$\tau = \frac{V}{v_0} = \frac{238 \text{ ft}^3}{476 \text{ ft}^3/\text{hr}} = 0.5 \text{ h}$$

We now solve these three equations simultaneously using POLYMATH. The program and output in graphical form are shown in Table E6-6.1 and Figure E6-6.1, respectively. However, I hasten to point out that these equations can be solved analytically and the solution was given in the first edition of this text.

The emergence of user-friendly ODE solvers favors this approach over fractional conversion

TABLE E6-6.1. POLYMATH PROGRAM

Equations	Initial Values
$d(ch)/d(t)=r1+r2$	0.021
$d(cm)/d(t)=r1$	0.0105
$d(cx)/d(t)=-r1+r2$	0
$k1=55.2$	
$k2=30.2$	
$r1=-k1*cm*(ch**0.5)$	
$r2=-k2*cx*(ch**0.5)$	
$t_0 = 0, \quad t_f = 0.5$	

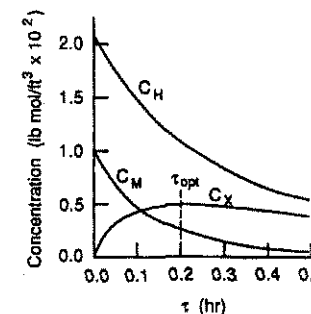


Figure E6-6.1 Concentration profiles in a PFR.

6.3.7 Multiple Reactions in a CSTR

For a CSTR, a coupled set of algebraic equations analogous to PFR differential equations must be solved.

$$V = \frac{F_{j0} - F_j}{-r_j} \quad (6-28)$$

Rearranging yields

$$F_{j0} - F_j = -r_j V \quad (6-29)$$

Recall that r_j in Equation (6-16) is a function (f_j) of the species concentrations

$$r_j = \sum_{i=1}^q r_{ij} = f_j(C_1, C_2, \dots, C_N) \quad (6-16)$$

After writing a mole balance on each species in the reaction set, we substitute for concentrations in the respective rate laws. If there is no volume change with reaction, we use concentrations, C_j , as variables. If the reactions are

gas-phase and there is volume change, we use molar flow rates, F_j , as variables. The total molar flow rate for n species is

$$F_T = \sum_{j=1}^n F_j \quad (6-30)$$

For q reactions occurring in the gas phase, where N different species are present, we have the following set of algebraic equations:

$$F_{I0} - F_I = -r_I V = V \sum_{i=1}^q -r_{iI} = V \cdot f_I \left(\frac{F_1}{F_T} C_{T0}, \dots, \frac{F_N}{F_T} C_{T0} \right) \quad (6-31)$$

$$F_{j0} - F_j = -r_j V = V \cdot f_j \left(\frac{F_1}{F_T} C_{T0}, \dots, \frac{F_N}{F_T} C_{T0} \right) \quad (6-32)$$

$$F_{N0} - F_N = -r_N V = V \cdot f_N \left(\frac{F_1}{F_T} C_{T0}, \dots, \frac{F_N}{F_T} C_{T0} \right) \quad (6-33)$$

We can use an equation solver in POLYMATH or similar to solve Equations (6-31) through (6-33).

Example 6-7 Hydrodealkylation of Mesitylene in a CSTR

For the multiple reactions and conditions described in Example 6-6, calculate the conversion of hydrogen and mesitylene along with the exiting concentrations of mesitylene, hydrogen, and xylene in a CSTR.

Solution

1. Mole balances:

$$\text{Hydrogen: } F_{H0} - F_H = (-r_{1H} - r_{2H}) V \quad (E6-7.1)$$

$$\text{Mesitylene: } F_{M0} - F_M = -r_{1M} V \quad (E6-7.2)$$

$$\text{Xylene: } F_X = (r_{1X} + r_{2X}) V \quad (E6-7.3)$$

$$\text{Toluene: } F_T = r_{2T} V \quad (E6-7.4)$$

$$\text{Methane: } F_{Me} = (r_{1Me} + r_{2Me}) V \quad (E6-7.5)$$

2. Rate laws:

$$\text{Reaction 1: } -r_{1H} = -r_{1M} = r_{1X} = r_{1Me} = k_1 C_H^{1/2} C_M \quad (E6-7.6)$$

$$\text{Reaction 2: } -r_{2H} = -r_{2X} = r_{2T} = r_{2Me} = k_2 C_H^{1/2} C_X \quad (E6-7.7)$$

3. Stoichiometry ($v = v_0$):

$$(E6-7.8)$$

$$F_H = v_0 C_H \quad (E6-7.9)$$

$$F_M = v_0 C_M \quad (E6-7.10)$$

$$F_X = v_0 C_X \quad (E6-7.11)$$

$$F_T = v_0 C_T = (F_{M0} - F_M) - F_X \quad (E6-7.12)$$

$$F_{Me} = v_0 C_{Me} = v_0 (C_{H0} - C_H) \quad (E6-7.13)$$

4. Combining and letting $\tau = V/v_0$ (space-time) yields:

$$C_{H0} - C_H = (k_1 C_H^{1/2} C_M + k_2 C_H^{1/2} C_X) \tau \quad (E6-7.14)$$

$$C_{M0} - C_M = (k_1 C_H^{1/2} C_M) \tau \quad (E6-7.15)$$

$$C_X = (k_1 C_H^{1/2} C_M - k_2 C_H^{1/2} C_X) \tau \quad (E6-7.16)$$

Next, we put these equations in a form such that they can be readily solved using POLYMATH.

$$f(C_H) = 0 = C_H - C_{H0} + (k_1 C_H^{1/2} C_M + k_2 C_H^{1/2} C_X) \tau \quad (E6-7.17)$$

$$f(C_M) = 0 = C_M - C_{M0} + k_1 C_H^{1/2} C_M \tau \quad (E6-7.18)$$

$$f(C_X) = 0 = (k_1 C_H^{1/2} C_M - k_2 C_H^{1/2} C_X) \tau - C_X \quad (E6-7.19)$$

The POLYMATH program and solution are shown in Table E6-7.1. The problem was solved for different values of τ and the results are plotted in Figure E6-7.1.

For a space-time of $\tau = 0.5$, the exiting concentrations are $C_H = 0.0089$, $C_M = 0.0029$, and $C_X = 0.0033$. The overall conversion is

$$\text{Hydrogen: } X_M = \frac{F_{H0} - F_H}{F_{H0}} = \frac{C_{H0} - C_H}{C_{H0}} = \frac{0.021 - 0.0089}{0.021} = 0.58$$

$$\text{Mesitylene: } X_H = \frac{F_{M0} - F_M}{F_{M0}} = \frac{C_{M0} - C_M}{C_{M0}} = \frac{0.0105 - 0.0029}{0.0105} = 0.72$$

TABLE E6-7.1. POLYMATH PROGRAM AND SOLUTION

Equations	Initial Values
$f(ch) = ch - .021 + (.55 \cdot 2 \cdot cm \cdot ch^{.5} \cdot 5 + 30 \cdot 2 \cdot cx \cdot ch^{.5} \cdot 5) \cdot \tau$	0.008
$f(cm) = cm - .0105 + (.55 \cdot 2 \cdot cm \cdot ch^{.5} \cdot 5) \cdot \tau$	0.0033
$f(cx) = (.55 \cdot 2 \cdot cm \cdot ch^{.5} \cdot 5 - 30 \cdot 2 \cdot cx \cdot ch^{.5} \cdot 5) \cdot \tau - cx$	0.005
$\tau = 0.5$	

To vary τ_{CSTR}
one can vary
either v_0 for a
fixed V or vary V
for a fixed v_0

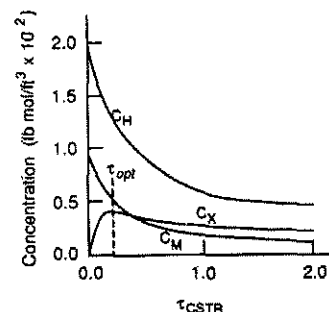


Figure E6-7.1 Concentrations as a function of space time.

We resolve Equations (E6-7.17) through (E6-7.19) for different values of τ to arrive at Figure E6-7.1.

The moles of hydrogen consumed in reaction 1 are equal to the moles of mesitylene consumed. Therefore, the conversion of hydrogen in reaction 1 is

$$X_{1H} = \frac{C_{M0} - C_M}{C_{H0}} = \frac{0.0105 - 0.0029}{0.021} = X_{1H} = 0.36$$

The conversion of hydrogen in reaction 2 is

$$X_{2H} = X_H - X_{1H} = 0.58 - 0.36 = 0.22$$

Next, we determine the selectivity and yield. First, consider the rate selectivity parameter, S_{XT} , at the optimum space-time. At τ_{opt} (see Figure E6-7.1), the concentration of xylene is a maximum. Therefore,

$$\frac{dC_X}{d\tau} = 0 = r_X$$

Thus, the rate (i.e., instantaneous) selectivity parameter of xylene relative to toluene is

$$S_{XT} = \frac{r_X}{r_T} = \frac{0}{r_T} = 0$$

Similarly, the xylene yield based on reaction rates is also zero. Consequently, we see that under these conditions (τ_{opt}) the instantaneous selectivity and instantaneous yield, which are based on reaction rates, are not very meaningful parameters and we must use the overall selectivity \tilde{S}_{XT} and the overall yield \tilde{Y}_{XT} , which are based on molar flow rates. The yield of xylene from mesitylene based on molar flow rates exiting the CSTR for $\tau = 0.5$ is

$$\tilde{Y}_{MX} = \frac{F_X}{F_{M0} - F_M} = \frac{C_X}{C_{M0} - C_M} = \frac{0.00313}{0.0105 - 0.0029}$$

$$\tilde{Y}_{MX} = \frac{0.41 \text{ mol xylene produced}}{\text{mole mesitylene reacted}}$$

Overall selectivity,
 \tilde{S} , and yield, \tilde{Y} .

The overall selectivity of xylene relative to toluene is

$$\tilde{S}_{XT} = \frac{F_X}{F_T} = \frac{C_X}{C_T} = \frac{C_X}{C_{M0} - C_M - C_X} = \frac{0.00313}{0.0105 - 0.0029 - 0.00313}$$

$$\tilde{S}_{XT} = \frac{0.7 \text{ mol xylene produced}}{\text{mole toluene produced}}$$

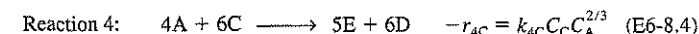
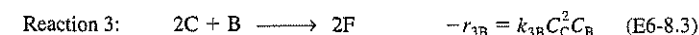
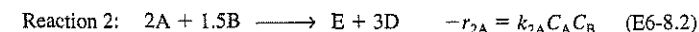
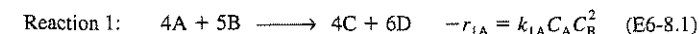
In the two preceding examples there was no volume change with reaction; consequently, we could use concentration as our dependent variable. We now consider a gas-phase reaction with volume change taking place in a PFR. Under these conditions, we must use the molar flow rates as our dependent variables.

Example 6-8 Calculating Concentrations as Functions of Position for NH_3 Oxidation in a PFR

The following gas-phase reactions take place simultaneously on a metal oxide-supported catalyst:

1. $4\text{NH}_3 + 5\text{O}_2 \longrightarrow 4\text{NO} + 6\text{H}_2\text{O}$
2. $2\text{NH}_3 + 1.5\text{O}_2 \longrightarrow \text{N}_2 + 3\text{H}_2\text{O}$
3. $2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2$
4. $4\text{NH}_3 + 6\text{NO} \longrightarrow 5\text{N}_2 + 6\text{H}_2\text{O}$

Writing these equations in terms of symbols yields



$$\text{with}^7 \quad k_{1A} = 5.0 \text{ (m}^3/\text{kmol)}^2/\text{min} \quad k_{2C} = 2.0 \text{ m}^3/\text{kmol} \cdot \text{min}$$

$$k_{3B} = 10.0 \text{ (m}^3/\text{kmol)}^2/\text{min} \quad k_{4C} = 5.0 \text{ (m}^3/\text{kmol)}^{2/3}/\text{min}$$

Note: We have converted the specific reaction rates to a per unit volume basis by multiplying the k' on a per mass of catalyst basis by the bulk density of the packed bed.

Determine the concentrations as a function of position (i.e., volume) in a PFR.

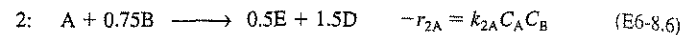
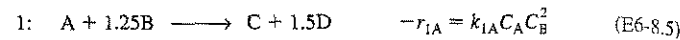
Additional information: Feed rate = 10 dm³/min; volume of reactor = 10 dm³; and

$$C_{A0} = C_{B0} = 1.0 \text{ mol/dm}^3$$

⁷ Reaction orders and rate constants were estimated from pericosity measurements for a bulk catalyst density of 1.2 kg/m³.

Solution

First, we divide each equation through by the stoichiometric coefficient of the species for which the rate law is given:



Stoichiometry. We will express the concentrations in terms of the molar flow rates:

$$C_j = \frac{F_j}{F_T} C_{T0}$$

and then substitute for the concentration of each reaction species in the rate laws. Writing the rate law for species A in reaction 1 in terms of the rate of formation, r_{1A} , and molar flow rates, F_A and F_B we obtain

$$r_{1A} = -k_{1A} C_A C_B^2 = -k_{1A} \left(C_{T0} \frac{F_A}{F_T} \right) \left(C_{T0} \frac{F_B}{F_T} \right)^2$$

Thus

$$r_{1A} = -k_{1A} C_{T0}^3 \frac{F_A F_B^2}{F_T^3} \quad (\text{E6-8.9})$$

Similarly for the other reactions,

$$r_{2A} = -k_{2A} C_{T0}^2 \frac{F_A F_B}{F_T^2} \quad (\text{E6-8.10})$$

$$r_{3B} = -k_{3B} C_{T0}^3 \frac{F_C^2 F_B}{F_T^3} \quad (\text{E6-8.11})$$

$$r_{4C} = -k_{4C} C_{T0}^{5/3} \frac{F_C F_A^{2/3}}{F_T^{5/3}} \quad (\text{E6-8.12})$$

Next, we determine the *net* rate of reaction for each species by using the appropriate stoichiometric coefficients and then summing the rates of the individual reactions.

Net rates of formation:

$$\text{Species A:} \quad r_A = r_{1A} + r_{2A} + \frac{2}{3} r_{4C} \quad (\text{E6-8.13})$$

$$\text{Species B:} \quad r_B = 1.25 r_{1A} + 0.75 r_{2A} + r_{3B} \quad (\text{E6-8.14})$$

$$\text{Species C:} \quad r_C = -r_{1A} + 2 r_{3B} + r_{4C} \quad (\text{E6-8.15})$$

$$\text{Species D:} \quad r_D = -1.5 r_{1A} - 1.5 r_{2A} - r_{4C} \quad (\text{E6-8.16})$$

$$\text{Species E:} \quad r_E = -\frac{r_{2A}}{2} - \frac{5}{6} r_{4C} \quad (\text{E6-8.17})$$

$$\text{Species F:} \quad r_F = -2 r_{3B} = 2 k_{3B} C_C^2 C_B \quad (\text{E6-8.18})$$

Finally, we write mole balances on each species.

Mole balances:

$$\text{Species A:} \quad \frac{dF_A}{dV} = r_A = r_{1A} + r_{2A} + \frac{2}{3} r_{4C} \quad (\text{E6-8.19})$$

$$\text{Species B:} \quad \frac{dF_B}{dV} = r_B = 1.25 r_{1A} + 0.75 r_{2A} + r_{3B} \quad (\text{E6-8.20})$$

$$\text{Species C:} \quad \frac{dF_C}{dV} = r_C = -r_{1A} + 2 r_{3B} + r_{4C} \quad (\text{E6-8.21})$$

$$\text{Species D:} \quad \frac{dF_D}{dV} = r_D = -1.5 r_{1A} - 1.5 r_{2A} - r_{4C} \quad (\text{E6-8.22})$$

$$\text{Species E:} \quad \frac{dF_E}{dV} = r_E = -\frac{r_{2A}}{2} - \frac{5}{6} r_{4C} \quad (\text{E6-8.23})$$

$$\text{Species F:} \quad \frac{dF_F}{dV} = r_F = -2 r_{3B} \quad (\text{E6-8.24})$$

$$\text{Total:} \quad F_T = F_A + F_B + F_C + F_D + F_E + F_F \quad (\text{E6-8.25})$$

Combining

Rather than combining the concentrations, rate laws, and mole balances to write everything in terms of the molar flow rate as we did in the past, it is more convenient here to write our computer solution (either POLYMATH or our own program) using equations for r_{1A} , F_A , and so on. Consequently, we shall write Equations (E6-8.9) through (E6-8.12) and (E6-8.19) through (E6-8.25) as individual lines and let the computer combine them to obtain a solution.

The corresponding POLYMATH program written for this problem is shown in Table E6-8.1 and a plot of the output is shown in Figure E6-8.1. One notes that there is a maximum in the concentration of NO (i.e., C) at approximately 1.5 dm³.

Solutions to these equations are most easily obtained with an ODE solver

TABLE E6-8.1. POLYMATH PROGRAM

Equations	Initial Values
$d(fb)/d(v) = 1.25 \cdot r1a + .75 \cdot r2a + r3b$	1.0
$d(fa)/d(v) = r1a + r2a + 2 \cdot r4c/3$	1.0
$d(fc)/d(v) = -r1a + 2 \cdot r3b + r4c$	0
$d(fd)/d(v) = -1.5 \cdot r1a - 1.5 \cdot r2a - r4c$	0
$d(fe)/d(v) = .5 \cdot r2a - 5 \cdot r4c/6$	0
$d(ff)/d(v) = -2 \cdot r3b$	0
$ft = fa + fb + fc + fd + fe + ff$	
$r1a = -5 \cdot 8 \cdot (fa/ft) \cdot (fb/ft) \cdot 2$	
$r2a = -2 \cdot 4 \cdot (fa/ft) \cdot (fb/ft)$	
$r4c = -5 \cdot 3.175 \cdot (fc/ft) \cdot (fa/ft) \cdot (2/3)$	
$r3b = -10 \cdot 8 \cdot (fc/ft) \cdot 2 \cdot (fb/ft)$	
$ca = 2 \cdot fa/ft$	
$v_0 = 0, \quad v_f = 10$	

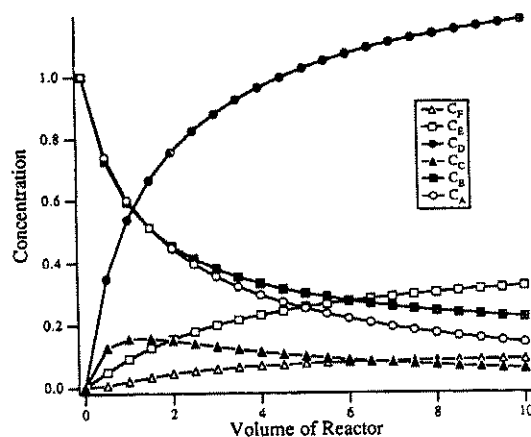


Figure E6-8.1 Concentration profiles.

However, there is one fly in the ointment here: It may not be possible to determine the rate laws for each of the reactions. In this case it may be necessary to work with the minimum number of reactions and hope that a rate law can be found for each reaction. That is, you need to find the number of linearly independent reactions in your reaction set. In Example 6-8 just discussed, there are four reactions given [(E6-8.5) through (E6-8.8)]. However, only three of these reactions are independent, as the fourth can be formed from a linear combination of the other three. Techniques for determining the number of independent reactions are given by Aris.⁸

⁸ R. Aris, *Elementary Chemical Reactor Analysis* (Upper Saddle River, N.J.: Prentice Hall, 1969).

6.4 Sorting It All Out

In Example 6-8 we were given the rate laws and asked to calculate the product distribution. The inverse of the problem described in Example 6-8 must frequently be solved. Specifically, the rate laws often must be determined from the variation in the product distribution generated by changing the feed concentrations. In some instances this determination may not be possible without carrying out independent experiments on some of the reactions in the sequence. The best strategy to use to *sort out* all of the rate law parameters will vary from reaction sequence to reaction sequence. Consequently, the strategy developed for one system may not be the best approach for other multiple-reaction systems. One general rule is to start an analysis by looking for species produced in only one reaction; next, study the species involved in only two reactions, then three, and so on.

When the intermediate products (e.g., species C) are free radicals, it may not be possible to perform independent experiments to determine the rate law parameters. Consequently, we must deduce the rate law parameters from changes in the distribution of reaction products with feed conditions. Under these circumstances, the analysis turns into an optimization problem to estimate the best values of the parameters that will minimize the sums of the squares between the calculated variables and measured variables. This process is basically the same as that described in Section 5.4.2, but more complex, owing to the larger number of parameters to be determined. We begin by estimating the 12 parameter values using some of the methods just discussed. Next, we use our estimates to use nonlinear regression techniques to determine the best estimates of our parameter values from the data for all of the experiments.⁹ Software packages such as SimuSolv¹⁰ are becoming available for an analysis such as this one.

Nonlinear
least-squares

6.5 The Fun Part

I'm not talking about fun you can have at an amusement park, but CRE fun. Now that we have an understanding on how to solve for the exit concentrations of multiple reactions in a CSTR and how to plot the species concentration down the length of a PFR or PBR, we can address one of the most important and fun areas of chemical reaction engineering. This area, discussed in Section 6.1, is learning how to maximize the desired product and minimize the undesired product. It is this area that can make or break a chemical process financially. It is also an area that requires creativity in designing the reactor schemes and feed conditions that will maximize profits. Here you can mix and match reactors, feed streams, and side streams as well as vary the ratios of feed concentration in order to maximize or minimize the selectivity of a particular species. Problems of this type are what I call *digital-age problems*¹¹ because

⁹ See, for example, Y. Bard, *Nonlinear Parameter Estimation*, (Academic Press, San Diego, Calif.: 1974).

¹⁰ The SimuSolv Computer Program is a proprietary product of The Dow Chemical Company that is leased with restricted rights according to license terms and conditions. SimuSolv is a trademark of The Dow Chemical Company.

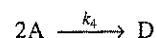
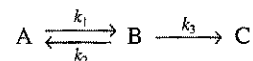
¹¹ H. Scott Fogler, *Teaching Critical Thinking, Creative Thinking, and Problem Solving in the Digital Age*, Phillips Lecture (Stillwater, Okla.: OSU Press, 1997).

we normally need to use ODE solvers along with critical and creative thinking skills to find the best answer. A number of problems at the end of this chapter will allow you to practice these critical and creative thinking skills. These problems offer opportunity to explore many different solution alternatives to enhance selectivity and have fun doing it.

However, to carry CRE to the next level and to have a lot more fun solving multiple reaction problems, we will have to be patient a little longer. The reason is that in this chapter we consider only isothermal multiple reactions, and it is nonisothermal multiple reactions where things really get interesting. Consequently, we will have to wait to carry out schemes to maximize the desired product in nonisothermal multiple reactions until we study heat effects in Chapters 8 and 9. After studying these chapters we will add a new dimension to multiple reactions, as we now have another variable, temperature, that we may or may not be able to use to affect selectivity and yield. One particularly interesting **problem (P8-30)** we will study is the production of styrene from ethylbenzene in which two side reactions, one endothermic, and one exothermic, must be taken into account. Here we may vary a whole slew of variables, such as entering temperature, diluent rate, and observe optima, in the production of styrene. However, we will have to delay gratification of the styrene study until we have mastered Chapter 8.

6.6 The Attainable Region

A technique developed by Professors Glasser and Hildebrandt¹² allows one to find the optimum reaction system for certain types of rate laws. The WWW¹² uses modified van de Vusse kinetics, that is,



to illustrate what combination of reactors PFR/CSTR should be used to obtain the maximum amount of B. The combined mole balance and rate laws for these liquid phase reactions can be written in terms of space-time as

van de Vusse
kinetics

$$\frac{dC_A}{d\tau} = -k_1 C_A + k_2 C_B - k_4 C_A^2$$

$$\frac{dC_B}{d\tau} = k_1 C_A - k_2 C_B - k_3 C_B$$

$$\frac{dC_C}{d\tau} = k_3 C_B$$

$$\frac{dC_D}{d\tau} = \frac{k_4}{2} C_A^2$$

PFR

¹²Department of Chemical Engineering, Witswatersrand University, Johannesburg, South Africa. See also D. Glasser, D. Hildebrandt, and C. Crowe, *IEC Res.*, 26, 1803 (1987). <http://www.engin.umich.edu/~cre/Chapters/ARpages/Intro/intro.htm> and <http://sunsite.wits.ac.za/wits/fac/engineering/procmat/ARHomepage/frame.htm>

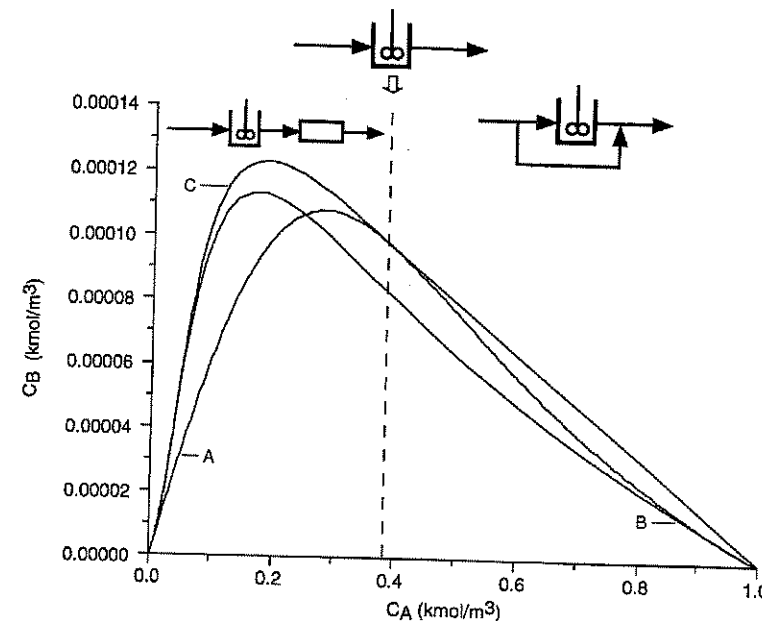


Figure 6-5 Phase plane plots of C_B as a function of C_A .

One can solve this set of ODEs to obtain the plot of C_B as a function of C_A shown in Figure 6-5.

In a similar fashion one can solve the combined CSTR mole balances and rate laws, that is,

CSTR

$$C_{A0} - C_A = \tau[k_1 C_A - k_2 C_B + k_4 C_A^2]$$

$$C_B = \tau[k_1 C_A - k_2 C_B - k_3 C_B]$$

These equations can be solved to give C_A and C_B as a function of space time and also C_B as a function of C_A . The latter is shown as the dashed line in Figure 6-5.

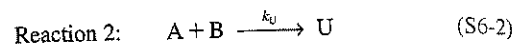
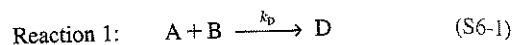
The values of the specific reaction rates or $k_1 = 0.01 \text{ s}^{-1}$, $k_2 = 5 \text{ s}^{-1}$, $k_3 = 10 \text{ s}^{-1}$, $k_4 = 100 \frac{\text{m}^3}{\text{kmol} \cdot \text{s}}$

The WWW¹² shows how to use these plots along with the attainable region technique to maximize the amount of B produced.

From Figure 6-5, we see that if the space-time is such that the effluent concentration of A is between 0.38 and 1.0 kmol/m³, a CSTR with by-pass will give us the maximum concentration of B. If the effluent concentration A is exactly 0.38, then a single CSTR is the best choice. Finally, if the total space-time ($\tau = \tau_{\text{PFR}} + \tau_{\text{CSTR}}$) is such that the effluent concentration is below 0.38 kmol/m³, then a CSTR followed by a PFR will give the maximum amount of B.

SUMMARY

For the competing reactions



1. Typical rate expressions are

$$r_D = A_D e^{-E_D/RT} C_A^{\alpha_1} C_B^{\beta_1} \quad (\text{S6-3})$$

$$r_U = A_U e^{-E_U/RT} C_A^{\alpha_2} C_B^{\beta_2} \quad (\text{S6-4})$$

and the instantaneous selectivity parameter is defined as

$$S_{DU} = \frac{r_D}{r_U} = \frac{A_D}{A_U} \exp\left(-\frac{(E_D - E_U)}{RT}\right) C_A^{\alpha_1 - \alpha_2} C_B^{\beta_1 - \beta_2} \quad (\text{S6-5})$$

- If $E_D > E_U$, the selectivity parameter S_{DU} will increase with increasing temperature.
 - If $\alpha_1 > \alpha_2$ and $\beta_2 > \beta_1$, the reaction should be carried out at high concentrations of A and low concentrations of B to maintain the selectivity parameter S_{DU} at a high value. Use a semibatch reactor with pure A initially or a tubular reactor in which B is fed at different locations down the reactor. Other cases discussed in the text are $\alpha_1 > \alpha_2$, $\beta_2 > \beta_1$ and $\alpha_1 > \alpha_2$, $\beta_1 > \beta_2$.
2. The *instantaneous yield* at a point is defined as the ratio of the rate of formation of a specified product D to the rate of depletion of the key reactant A:

$$Y_D = \frac{r_D}{-r_A} = \frac{r_D}{-r_{A1} - r_{A2}} \quad (\text{S6-6})$$

The overall yield is the ratio of the number of moles of a product at the end of a reaction to the number of moles of the key reactant that have been consumed:

$$\bar{Y}_D = \frac{N_D}{N_{A0} - N_A} \quad (\text{S6-7})$$

For a flow system, this yield is

$$\bar{Y}_D = \frac{F_D}{F_{A0} - F_A} \quad (\text{S6-8})$$

The overall selectivity, based on molar flow rates leaving the reactor, for the reactions given by Equations (S6-1) and (S6-2) is

$$\bar{S}_{DU} = \frac{F_D}{F_U} \quad (\text{S6-9})$$

3. The algorithm:

Mole balances:

$$\frac{dF_j}{dV} = r_j \quad \text{PFR} \quad (\text{S6-10})$$

$$F_{j0} - F_j = -r_j V \quad \text{CSTR} \quad (\text{S6-11})$$

$$\frac{dN_j}{dt} = r_j V \quad \text{Batch} \quad (\text{S6-12})$$

$$\frac{dC_j}{dt} = r_j - \frac{v_0(C_{j0} - C_j)}{V} \quad \text{Liquid-semibatch} \quad (\text{S6-13})$$

Rate laws:

$$r_{ij} = k_{ij} f_i(C_1, C_j, C_n) \quad (\text{S6-14})$$

Stoichiometry:

$$F_T = \sum_{j=1}^n F_j \quad (\text{S6-15})$$

$$r_j = \sum_{i=1}^q r_{ij} \quad (\text{S6-16})$$

$$\frac{r_{iA}}{-a_i} = \frac{r_{iB}}{-b_i} = \frac{r_{iC}}{c_i} = \frac{r_{iD}}{d_i} \quad (\text{S6-17})$$

Gas phase:

$$C_j = C_{T0} \frac{F_j}{F_T} \frac{P}{P_0} \frac{T_0}{T} \quad (\text{S6-18})$$

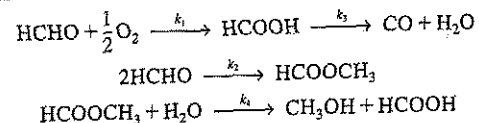
$$\frac{dP}{dW} = -\frac{\alpha}{2} \left(\frac{T}{T_0} \right) \frac{P_0}{P/P_0} \left(\frac{F_T}{F_{T0}} \right) \quad (\text{4-28})$$

Let $y = P/P_0$:

$$\frac{dy}{dW} = -\frac{\alpha}{2y} \left(\frac{F_T}{F_{T0}} \right) \frac{T}{T_0} \quad (\text{S6-19})$$

O.D.E. SOLVER ALGORITHM

MULTIPLE ELEMENTARY REACTIONS IN A PFR



Let A = HCHO, B = O₂, C = HCOOH, D = HCOOCH₃, E = CO, W = H₂O, G = CH₃OH

$$\frac{dF_A}{dV} = -k_1 C_{T0}^{3/2} \left(\frac{F_A}{F_T}\right) \left(\frac{F_B}{F_T}\right)^{1/2} - k_2 C_{T0}^2 \left(\frac{F_A}{F_T}\right)^2$$

$$\frac{dF_B}{dV} = -\frac{k_1}{2} C_{T0}^{3/2} \left(\frac{F_A}{F_T}\right) \left(\frac{F_B}{F_T}\right)^{1/2}$$

$$\frac{dF_C}{dV} = k_1 C_{T0}^{3/2} \left(\frac{F_A}{F_T}\right) \left(\frac{F_B}{F_T}\right)^{1/2} - k_3 C_{T0}^2 \left(\frac{F_C}{F_T}\right) + k_4 C_{T0}^2 \left(\frac{F_W}{F_T}\right) \left(\frac{F_D}{F_T}\right)$$

$$\frac{dF_D}{dV} = \frac{k_2}{2} C_{T0}^2 \left(\frac{F_A}{F_T}\right)^2 - k_4 C_{T0}^2 \left(\frac{F_D}{F_T}\right) \left(\frac{F_W}{F_T}\right)$$

$$\frac{dF_E}{dV} = k_2 C_{T0}^2 \left(\frac{F_C}{F_T}\right)$$

$$\frac{dF_W}{dV} = k_3 C_{T0}^2 \left(\frac{F_C}{F_T}\right) - k_4 C_{T0}^2 \left(\frac{F_W}{F_T}\right) \left(\frac{F_D}{F_T}\right)$$

$$\frac{dF_G}{dV} = k_4 C_{T0}^2 \left(\frac{F_W}{F_T}\right) \left(\frac{F_D}{F_T}\right)$$

$$F_T = F_A + F_B + F_C + F_D + F_E + F_W + F_G$$

$$F_{A0} = 10, F_{B0} = 5, V_F = 1000, k_1 C_{T0}^{3/2} = 0.04, k_2 C_{T0}^2 = 0.007, k_3 C_{T0}^2 = 0.014, k_4 C_{T0}^2 = 0.45$$

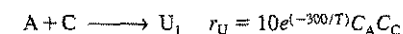
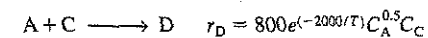
QUESTIONS AND PROBLEMS

The subscript to each of the problem numbers indicates the level of difficulty: A, least difficult; D, most difficult.

A = ● B = ■ C = ◆ D = ♦♦

In each of the questions and problems below, rather than just drawing a box around your answer, write a sentence or two describing how you solved the problem, the assumptions you made, the reasonableness of your answer, what you learned, and any other facts that you want to include. You may wish to refer to W. Strunk and E. B. White, *The Elements of Style* (New York: Macmillan, 1979), and Joseph M. Williams, *Style: Ten Lessons in Clarity & Grace* (Glenview, Ill.: Scott, Foresman, 1989) to enhance the quality of your sentences.

- P6-1** Make up and solve an original problem to illustrate the principles of this chapter. See Problem P4-1 for guidelines.
- P6-2** (a) What if you could vary the temperature in Example 6-1? What temperature and CSTR space-time would you use to maximize \bar{Y}_D for an entering concentration of A of 1 mol/dm³? What temperature would you choose?
- (b) What if the reactions in Example 6-3 were carried out in a CSTR instead of a PBR? What would be the corresponding optimum conversion and space-time, τ_{opt} ?
- (c) What if you varied the catalyst size in Example 6-6? Would it increase or decrease \bar{S}_{XT} ? [Hint: Use a form of Equation (S6-18) and make a plot of \bar{S}_{XT} versus α .]
- (d) What feed conditions and reactors or combination of reactors shown in Figure 6-3 would you use to
- (1) maximize the overall selectivity \bar{S}_{CF} in Example 6-8? Start by plotting \bar{S}_{CF} as a function of Θ_B in a 10-dm³ PFR;
 - (2) maximize the yield of Y_{FA} with and the overall selectivity of \bar{S}_{FC} ?
- (e) What if you could vary the ratio of hydrogen to mesitylene in the feed ($0.2 < \Theta_H < 5$) in Example 6-6. What is the effect of Θ_H on τ_{opt} ? Plot the optimum yield of xylene as a function of Θ_H . Plot the selectivity \bar{S}_{XT} as a function of Θ_H . Suppose that the reactions could be run at different temperatures. What would be the effect of the ratio of k_1 to k_2 on τ_{opt} and on the selectivity \bar{S}_{XT} and the yield?
- (f) Repeat part (d) for Example 6-7.
- (g) How would pressure drop affect the results shown in Figure E6-8.1?
- P6-3_B** The hydrogenation of *o*-cresol 2-methylphenol (MP) is carried out over a Ni-catalyst [Ind. Eng. Chem. Res., 28, 693 (1989)] to form 2-methylcyclohexanone (ON), which then reacts to form two stereoisomers, *cis*- (cs-OL) and *trans* (tr-OL)-2-methylcyclohexanol. The equilibrium compositions (on a hydrogen-free basis) are shown in Figure P6-3.
- (a) Plot (sketch) the selectivities of ON to cs-OL and of tr-OL to cs-OL as a function of temperature in the range 100 to 300°C.
- (b) Estimate the heat of reaction for the isomerization
- $$\text{tr-OL} \rightleftharpoons \text{cs-OL}$$
- (c) Plot (sketch) the yields of MP to tr-OL and of MP to ON as functions of temperature assuming a stoichiometric feed.
- P6-4_A** (a) What reaction schemes and conditions would you use to maximize the selectivity parameters S for the following parallel reactions:



where D is the desired product and U_1 is the undesired product?

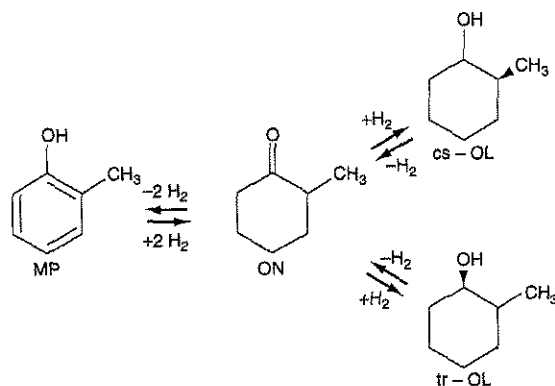
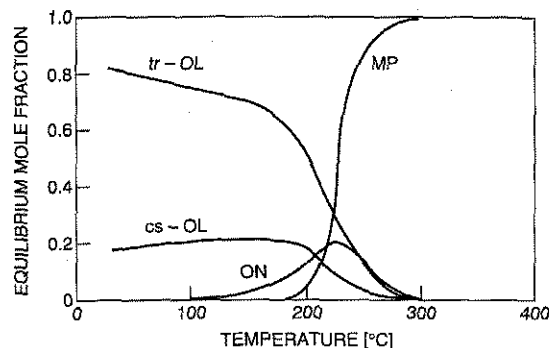
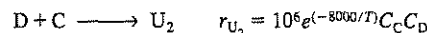


Figure P6-3 [Reprinted with permission from W. K. Schumann, O. K. Kut, and A. Baiker, *Ind. Eng. Chem. Res.*, 28, 693 (1989). Copyright © (1989) American Chemical Society.]

- (b) State how your answer to part (a) would change if C were to react with D to form another undesired product,

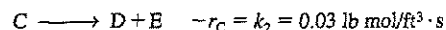


At what temperature should the reactor be operated if the concentrations of A and D in the reactor were 1 mol/dm³?

- (c) For a 2-dm³ laboratory CSTR with $C_{C0} = C_{A0} = 1$ mol/dm³ and $v_0 = 1$ dm³/min, what temperature would you recommend to maximize \bar{Y}_D ?
 (d) Two gas-phase reactions are occurring in a plug-flow tubular reactor, which is operated isothermally at a temperature of 440°F and a pressure of 5 atm. The first reaction is first-order:



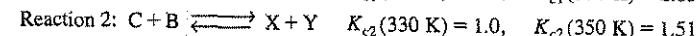
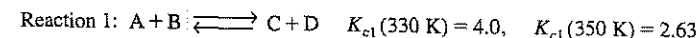
and the second reaction is zero-order:



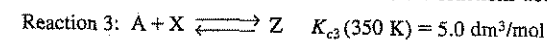
The feed, which is equimolar in A and C, enters at a flow rate of 10 lb mol/s. What reactor volume is required for a 50% conversion of A to B? (Ans.: $V = 105 \text{ ft}^3$.)

- P6-5_B A mixture of 50% A, 50% B is charged to a constant-volume batch reactor in which equilibrium is rapidly achieved. The initial total concentration is 3.0 mol/dm³.

- (a) Calculate the equilibrium concentrations and conversion of A at 330 K for the reaction sequence



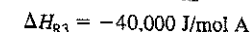
- (b) Suppose now the temperature is increased to 350 K. As a result, a third reaction must now be considered in addition to the reactions above:



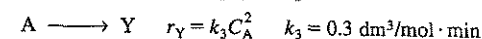
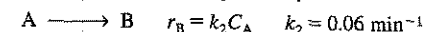
Calculate the equilibrium concentrations, conversion of A and overall selectivities \bar{S}_{CX} , \bar{S}_{DZ} , and \bar{S}_{YZ} .

- (c) Vary the temperature over the range 300 to 500 K to learn the effect of selectivities \bar{S}_{CX} , \bar{S}_{DZ} , and \bar{S}_{YZ} on temperature.

Additional information:



- P6-6_A Consider the following system of gas-phase reactions:



B is the desired product, and X and Y are foul pollutants that are expensive to get rid of. The specific reaction rates are at 27°C. The reaction system is to be operated at 27°C and 4 atm. Pure A enters the system at a volumetric flow rate of 10 dm³/min.

- (a) Sketch the instantaneous selectivities (S_{BX} , S_{BY} , and $S_{B/X+Y} = r_B/(r_X + r_Y)$) as a function of the concentration of C_A .
 (b) Consider a series of reactors. What should be the volume of the first reactor?
 (c) What are the effluent concentrations of A, B, X, and Y from the first reactor?
 (d) What is the conversion of A in the first reactor?
 (e) If 90% conversion of A is desired, what reaction scheme and reactor sizes should you use?
 (f) Suppose that $E_1 = 10,000 \text{ cal/mol}$, $E_2 = 20,000 \text{ cal/mol}$, and $E_3 = 30,000 \text{ cal/mol}$. What temperature would you recommend for a single CSTR with a space-time of 10 min and an entering concentration of A of 0.1 mol/dm³?

- P6-7_B Pharmacokinetics concerns the ingestion, distribution, reaction, and elimination reaction of drugs in the body. Consider the application of pharmacokinetics to one of the major problems we have in the United States, drinking and driving. Here we shall model how long one must wait to drive after having a tall martini. In most states the legal intoxication limit is 1.0 g of ethanol per liter of body fluid. (In Sweden it is 0.5 g/L, and in Eastern Europe and Russia it is any value above 0.0 g/L.) The ingestion of ethanol into the bloodstream



and subsequent elimination can be modeled as a series reaction. The rate of absorption from the gastrointestinal tract into the bloodstream and body is a first-order reaction with a specific reaction rate constant of 10 h^{-1} . The rate at which ethanol is broken down in the bloodstream is limited by regeneration of a coenzyme. Consequently, the process may be modeled as a zero-order reaction with a specific reaction rate of $0.192 \text{ g/h} \cdot \text{L}$ of body fluid. How long would a person have to wait (a) in the United States; (b) in Sweden; and (c) in Russia if they drank two tall martinis immediately after arriving at a party? How would your answer change if (d) the drinks were taken $\frac{1}{2}$ h apart; (e) the two drinks were consumed at a uniform rate during the first hour? (f) Suppose that one went to a party, had one and a half tall martinis right away, and then received a phone call saying an emergency had come up and they needed to drive home immediately. How many minutes would they have to reach home before he/she became legally intoxicated, assuming that the person had nothing further to drink? (g) How would your answers be different for a thin person? A heavy person? For each case make a plot of concentration as a function of time. (Hint: Base all ethanol concentrations on the volume of body fluid. Plot the concentration of ethanol in the blood as a function of time.)

Additional information:

Ethanol in a tall martini: 40 g

Volume of body fluid: 40 L

(SADD-MADD problem)

P6-8B

(Pharmacokinetics) Tarzlon is a liquid antibiotic that is taken orally to treat infections of the spleen. It is effective only if it can maintain a concentration in the blood-stream (based on volume of body fluid) above 0.4 mg per dm^3 of body fluid. Ideally, a concentration of 1.0 mg/dm^3 in the blood would like to be realized. However, if the concentration in the blood exceeds 1.5 mg/dm^3 , harmful side effects can occur. Once the Tarzlon reaches the stomach it can proceed in two pathways, both of which are first order: (1) It can be absorbed into the bloodstream through the stomach walls; (2) it can pass out through the gastrointestinal tract and not be adsorbed into the blood. Both these processes are first order in Tarzlon concentration in the stomach. Once in the bloodstream, Tarzlon attacks bacterial cells and is subsequently degraded by a zero-order process. Tarzlon can also be removed from the blood and excreted in urine through a first-order process within the kidneys. In the stomach:

Adsorption into blood $k_1 = 0.15 \text{ h}^{-1}$

Elimination through gastrointestinal $k_2 = 0.6 \text{ h}^{-1}$

In the bloodstream:

Degradation of Tarzlon $k_3 = 0.1 \text{ mg/dm}^3 \cdot \text{h}$

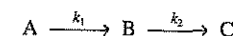
Elimination through urine $k_4 = 0.2 \text{ h}^{-1}$

- Plot the concentration of Tarzlon in the blood as a function of time when 1 dose (i.e. one liquid capsule) of Tarzlon is taken.
- How should the Tarzlon be administered (dosage and frequency) over a 48-h period to be most effective?
- Comment on the dose concentrations and potential hazards.
- How would your answers change if the drug were taken on a full or empty stomach?

One dose of Tarzlon is 250 mg, in liquid form: Volume of body fluid = 40 dm^3



P6-9B The elementary liquid-phase-series reaction



is carried out in a 500-dm^3 batch reactor. The initial concentration of A is 1.6 mol/dm^3 . The desired product is B and separation of the undesired product C is very difficult and costly. Because the reaction is carried out at a relatively high temperature, the reaction is easily quenched.

Additional information:

Cost of pure reactant A = $\$10/\text{mol A}$

Selling price of pure B = $\$50/\text{mol B}$

Separation cost of A from B = $\$50/\text{mol A}$

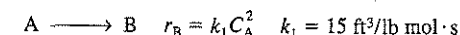
Separation cost of C from B = $\$30 (e^{0.5C} - 1)$

$k_1 = 0.4 \text{ h}^{-1}$

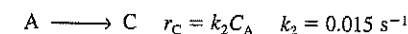
$k_2 = 0.01 \text{ h}^{-1}$ at 100°C

- Assuming that each reaction is irreversible, plot the concentrations of A, B, and C as a function of time.
- Calculate the time the reaction should be quenched to achieve the maximum profit.
- For a CSTR space-time of 0.5 h, what temperature would you recommend to maximize B? ($E_1 = 10,000 \text{ cal/mol}$, $E_2 = 20,000 \text{ cal/mol}$)
- Assume that the first reaction is reversible with $k_{-1} = 0.3 \text{ h}^{-1}$. Plot the concentrations of A, B, and C as a function of time.
- Plot the concentrations of A, B, and C as a function of time for the case where both reactions are reversible with $k_{-2} = 0.005 \text{ h}^{-1}$.
- Vary k_1 , k_2 , k_{-1} , and k_{-2} . Explain the consequence of $k_1 > 100$ and $k_2 < 0.1$ with $k_{-1} = k_{-2} = 0$ and with $k_{-2} = 1$, $k_{-1} = 0$, and $k_{-2} = 0.25$.
- Reconsider part (a) for reactions are carried out in a packed-bed reactor with 100 kg of catalyst for which $k_1 = 0.25 \text{ dm}^3/\text{kg cat} \cdot \text{min}$ and $k_2 = 0.15 \text{ dm}^3/\text{kg cat} \cdot \text{min}$. The flow is turbulent with $v_0 = 10 \text{ dm}^3$ and $C_{A0} = 1 \text{ mol/dm}^3$. It has been suggested to vary the particle size, keeping $W = 100 \text{ kg}$, in order to increase F_B , \bar{Y}_B , and \bar{S}_{BC} . If the particle size could be varied between 2 and 0.1 cm, what particle size would you choose? The pressure drop parameter for particles 1 cm in diameter is $\alpha = 0.00098 \text{ kg}^{-1}$. Is there a better way to improve the selectivity?

P6-10B You are designing a plug-flow reactor for the following gas-phase reaction:



Unfortunately, there is also a side reaction:



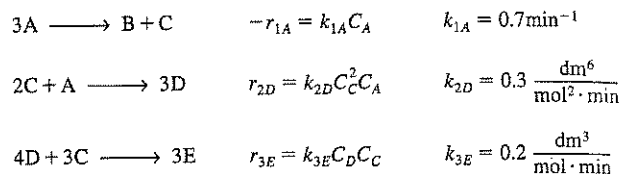
C is a pollutant and costs money to dispose of; B is the desired product.

- What size of reactor will provide an effluent stream at the maximum dollar value? B has a value of $\$60/\text{lb mol}$; it costs $\$15$ per lb mol to dispose of C. A has a value of $\$10$ per lb mol . (Ans.: $V = 896 \text{ ft}^3$.)
- Suppose that $E_1 = 10,000 \text{ Btu/lb mol}$ and $E_2 = 20,000 \text{ Btu/lb mol}$. What temperature (400 to 700°F) would you recommend for a 400-ft^3 CSTR?

Additional information:

Feed: 22.5 SCF/s of pure A
 Reaction conditions: 460°F, 3 atm pressure
 Volumetric flow rate: 15 ft³/s at reaction conditions
 Concentration of A in feed: 4.47×10^{-3} lb mol/ft³

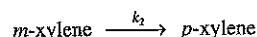
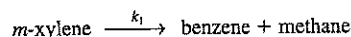
P6-11_B The following liquid-phase reactions were carried out in a CSTR at 325 K.



The concentrations measured *inside* the reactor were $C_A = 0.10$, $C_B = 0.93$, $C_C = 0.51$, and $C_D = 0.049$ all in mol/dm³.

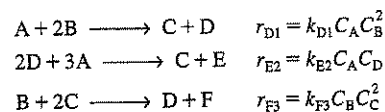
- What are r_{1A} , r_{2A} , and r_{3A} ? ($r_{1A} = -0.07$ mol/dm³·min)
- What are r_{1B} , r_{2B} , and r_{3B} ?
- What are r_{1C} , r_{2C} , and r_{3C} ? ($r_{1C} = 0.023$ mol/dm³·min)
- What are r_{1D} , r_{2D} , and r_{3D} ?
- What are r_{1E} , r_{2E} , and r_{3E} ?
- What are the net rates of formation of A, B, C, D, and E?
- The entering volumetric flow rate is 100 dm³/min and the entering concentration of A is 3 M. What is the CSTR reactor volume? (Ans.: 4000 dm³.)

P6-12 Calculating the space-time for parallel reactions. *m*-Xylene is reacted over a ZMS-5 zeolite catalyst. The following *parallel* elementary reactions were found to occur [Ind. Eng. Chem. Res., 27, 942 (1988)]:



- Calculate the space-time to achieve 90% conversion of *m*-xylene in a packed-bed reactor. Plot the overall selectivity and yields as a function of τ . The specific reaction rates are $k_1 = 0.22 \text{ s}^{-1}$ and $k_2 = 0.71 \text{ s}^{-1}$ at 673°C. A mixture of 75% *m*-xylene and 25% inerts is fed to a tubular reactor at volumetric flow rate of 2000 dm³/min and a total concentration of 0.05 mol/dm³. As a first approximation, neglect any other reactions such as the reverse reactions and isomerization to *o*-xylene.
- Suppose that $E_1 = 20,000$ cal/mol and $E_2 = 10,000$ cal/mol, what temperature would you recommend to maximize the formation of *p*-xylene in a CSTR with a space-time of 0.5 s?

P6-13_B The following liquid phase reactions are carried out isothermally in a 50 dm³ PFR:

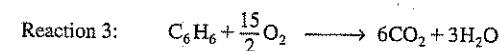
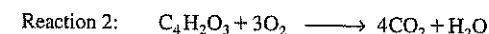
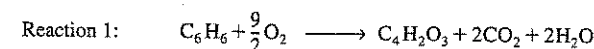


Additional information:

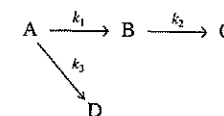
$$\begin{aligned} k_{D1} &= 0.25 \text{ dm}^6/\text{mol}^2 \cdot \text{min} & v_0 &= 10 \text{ dm}^3/\text{min} \\ k_{E2} &= 0.1 \text{ dm}^3/\text{mol} \cdot \text{min} & C_{A0} &= 1.5 \text{ mol/dm}^3 \\ k_{F3} &= 5.0 \text{ dm}^6/\text{mol}^2 \cdot \text{min} & C_{B0} &= 2.0 \text{ mol/dm}^3 \end{aligned}$$

- Plot the species concentrations and the conversion of A as a function of the distance (i.e., volume) down a 50-dm³ PFR. Note any maxima.
- Determine the effluent concentrations and conversion from a 50-dm³ CSTR. (Ans.: $C_A = 0.61$, $C_B = 0.79$, $C_F = 0.25$, and $C_D = 0.45$ mol/dm³)
- Plot the species concentrations and the conversion of A as a function of time when the reaction is carried out in a semibatch reactor initially containing 40 dm³ of liquid. Consider two cases: (1) A is fed to B, and (2) B is fed to A. What differences do you observe for these two cases?
- Vary the ratio of B to A ($1 < \Theta_B < 10$) in the feed to the PFR and describe what you find.

P6-14_B The production of maleic anhydride by the air oxidation of benzene was recently studied using a vanadium pentoxide catalyst [Chem. Eng. Sci., 43, 1051 (1988)]. The reactions that occur are:



Because these reactions were carried out in excess air, volume change with reaction can be neglected, and the reactions can be written symbolically as a pseudo-first-order reaction sequence



where A = benzene, B = maleic anhydride, C = products (H₂O, CO₂), D = products (CO₂, H₂O). The corresponding pseudo specific reaction rates, k_i , are (in all m³/kg cat · s):

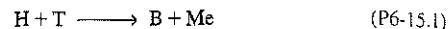
$$k_1 = 4280 \exp[-12,660/T(K)] \quad k_2 = 70,100 \exp[-15,000/T(K)]$$

$$k_3 = 26 \exp[-10,800/T(K)]$$

At 848 K, $k_1 = 1.4 \times 10^{-3}$, $k_2 = 1.46 \times 10^{-3}$, $k_3 = 7.65 \times 10^{-5}$. These reactions are carried out isothermally in both a CSTR and a PBR. Benzene enters the reactor at a concentration of 0.01 mol/dm³. The total volumetric flow rate is 0.0025 m³/s.

- Which reactions will dominate at low temperatures and which will dominate at high temperatures? For the sake of comparison, assume that 848 K is a moderate temperature.

- (b) For a catalytic weight of 50 kg, determine the exit concentrations from a "fluidized" CSTR at 848 K. (Ans.: $C_B = 0.3 \text{ mol/dm}^3$)
- (c) What is the selectivity of B to C and of B to D in the CSTR?
- (d) Plot the concentrations of all species as a function of PBR catalyst weight (up to 10 kg) assuming isothermal operation at 848 K.
- (e) What feed conditions and reactor or combinations of reactors shown in Figure 6-3 would you use to maximize the production of maleic anhydride?
- (f) How would your results in part (d) change if pressure drop were taken into account with $\alpha = 0.099 \text{ kg cat.}^{-1}$ in PBR? Make a plot similar to that in part (d) and describe any differences.
- P6-15_B** (a) Rework Examples 6-6 and 6-7 for the case where the toluene formed in reaction (E6-6.2) can also undergo hydrodealkylation to yield benzene, B:



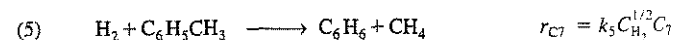
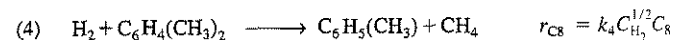
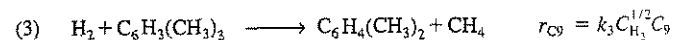
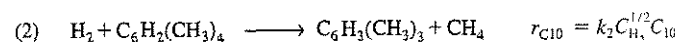
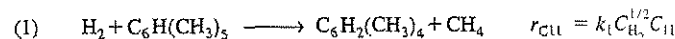
The rate law is

$$r_B = k_3 C_T C_H^{1/2} \quad (\text{P6-15.2})$$

with $k_3 = 11.2 (\text{ft}^3/\text{lb mol})^{0.5}/\text{h}$.

Include the concentrations of toluene and benzene in your results. The feed conditions given for Examples 6-6 and 6-7 apply to the case where all three reactions are taking place.

- (b) Vary the ratio of hydrogen to mesitylene ($1 < \Theta_H < 20$) and describe what you find.
- (c) What reactor schemes and feed conditions do you suggest to maximize \bar{S}_{XT} ? \bar{S}_{TB} ?
- (d) Suppose that the activation energies were $E_1 = 20,000 \text{ cal/mol}$, $E_2 = 10,000 \text{ cal/mol}$, and $E_3 = 30,000 \text{ cal/mol}$. What temperature would you recommend for the CSTR size in Example 6-7?
- P6-16_C** The following hydrodealkylation reactions occur over a Houdry Detol catalyst near 800 K and 3500 kPa:



$$k_5 = 2.1 (\text{kmol/m}^3)^{-1/2}/\text{s}$$

$$\frac{k_1}{k_5} = 17.6 \quad \frac{k_2}{k_5} = 10 \quad \frac{k_3}{k_5} = 4.4 \quad \frac{k_4}{k_5} = 2.7$$

The feed is equimolar in hydrogen and pentamethylbenzene.

- (a) For an entering volumetric flow rate of $1 \text{ m}^3/\text{s}$, what ratio of hydrogen to pentamethylbenzene and what PFR reactor volume would you recom-

mend to maximize the formation of $\text{C}_6\text{H}_4(\text{CH}_3)_2$ (i.e. C_8)? [Hint: Plot the overall selectivity as a function of reactor volume.]

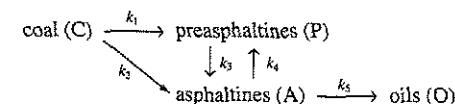
- (b) How would your answer change if you were to maximize the overall selectivity to C_8 to C_9 , i.e. \bar{S}_{89} ? To C_8 to C_7 ?
- (c) What do you think the point of this problem to be?

Make a plot of the mole fraction of each component as a function of conversion of pentamethylbenzene. Make a plot of the mole fraction of each component as a function of plug-flow reactor volume. Discuss any optimization that could be done.

- P6-17_B** Review the oxidation of formaldehyde to formic acid reactions over a vanadium titanium oxide catalyst [*Ind. Eng. Chem. Res.*, 28, 387 (1989)] shown in the ODE solver algorithm in the Summary.

- (a) Plot the species concentrations as a function of distance down the PFR for an entering flow rate of $100 \text{ dm}^3/\text{min}$ at 5 atm and 140°C . The feed is 66.7% HCHO and 33.3% O_2 . Note any maximum in species concentrations.
- (b) Plot the yield of overall HCOOH yield and overall selectivity of HCOH to CO, of HCOOCH_3 to CH_3OH and of HCOOH to HCOOCH_3 as a function of the Θ_{O_2} . Suggest some conditions to best produce formic acid. Write a paragraph describing what you find.
- (c) Compare your plot in part (a) with a similar plot when pressure drop is taken into account with $\alpha = 0.002 \text{ dm}^{-3}$.
- (d) Suppose that $E_1 = 10,000 \text{ cal/mol}$, $E_2 = 30,000 \text{ cal/mol}$, $E_3 = 20,000 \text{ cal/mol}$, and $E_4 = 10,000 \text{ cal/mol}$, what temperature would you recommend for a 1000-dm^3 PFR?

- P6-18_B** The liquefaction of Kentucky Coal No. 9 was carried out in a slurry reactor [D. D. Gertenbach, R. M. Baldwin, and R. L. Bain, *Ind. Eng. Chem. Process Des. Dev.*, 21, 490 (1982)]. The coal particles, which were less than 200 mesh, were dissolved in a -250°C vacuum cut of recycle oil saturated with hydrogen at 400°C . Consider the reaction sequence



which is a modified version of the one given by Gertenbach et al. All reactions are first order. Calculate the molar flow rate of each species as a function of space-time in

- (a) A plug-flow reactor.
(b) A 3-m^3 CSTR.

Additional information:

Entering concentration of coal: 2 kmol/m^3

Entering flow rate: $10 \text{ dm}^3/\text{min}$

At 400°F , $k_1 = 0.12 \text{ min}^{-1}$, $k_2 = 0.046 \text{ min}^{-1}$, $k_3 = 0.020 \text{ min}^{-1}$, $k_4 = 0.034 \text{ min}^{-1}$, $k_5 = 0.04 \text{ min}^{-1}$.

- P6-19_B** A liquid feed to a well-mixed reactor consists of 0.4 g mol/dm^3 of A and the same molar concentration of F. The product C is formed from A by two different reaction mechanisms: either by direct transformation or through intermediate B. The intermediate is also formed from F. Together with C, which remains in solution, an insoluble gas D is formed, which separates in the reactor.

All reaction steps are irreversible and first-order, except for the formation of B from F, which is second-order in F. The liquid carrier for reactants and products is an inert solvent, and no volume change results from the reaction:

$$\begin{aligned} k_1 &= 0.01 \text{ min}^{-1} & k_2 &= 0.02 \text{ min}^{-1} \\ k_3 &= 0.07 \text{ min}^{-1} & k_4 &= 0.50 \text{ dm}^3/\text{g mol} \cdot \text{min} \end{aligned}$$

$$\text{reactor volume} = 120 \text{ L}$$

- (a) What is the maximum possible molar concentration of C in the product?
 (b) If the feed rate is $2.0 \text{ dm}^3/\text{min}$, what is the yield of C (expressed as a percentage of the maximum), and what is the mole fraction of C in the product on a solvent-free basis? (Ans.: 0.583.)

(California Professional Engineers Exam)

P6-20_C The reaction sequence discussed in Example 6-8 is to be carried out in a microscale "fluidized" CSTR. The CSTR catalyst weight is 3 g. All of the conditions in the problem statement are the same except that the reaction is to be carried out at a slightly higher temperature and the rate constants are:

$$\begin{aligned} k_1 &= 10 \text{ m}^9/(\text{kmol}^2 \cdot \text{kg cat} \cdot \text{min}) & k_2 &= 4 \text{ m}^6/(\text{kmol} \cdot \text{kg cat} \cdot \text{min}) \\ k_3 &= 15 \text{ m}^9/(\text{kmol}^2 \cdot \text{kg cat} \cdot \text{min}) & k_4 &= 10 \text{ m}^3(\text{m}^3/\text{kmol})^{2/3}/\text{kg cat} \cdot \text{min} \end{aligned}$$

- (a) What are the exiting molar flow rates of each species.
 (b) What is the overall yield of
 (1) A to E?
 (2) B to F?
 (3) A to C?

P6-21_D (Flame retardants) We now reconsider a more comprehensive version of the combustion of CO discussed in P7-3. The reactions and their corresponding rate law parameters are given in Table P6-23. All reactions are assumed to be elementary [Combustion and Flame, 69, 113 (1987)]. The precombustion compositions (mol %) are:

TABLE P6-21 RATE LAW PARAMETERS

Reaction	Rate Parameters, $k = AT^n \exp(-E/RT)$ (cm^3 , s, cal, mol units)		
	A	n	E
A. Uninhibited			
1. $\text{OH} + \text{CO} \rightarrow \text{CO}_2 + \text{H}$	4.40E06	1.5	-740
2. $\text{CO} + \text{O} + \text{M} \rightarrow \text{CO}_2 + \text{M}$	5.30E13	0	-4,538
3. $\text{H} + \text{O}_2 \rightarrow \text{O} + \text{OH}$	1.20E17	-0.91	16,504
4. $\text{O} + \text{H}_2 \rightarrow \text{H} + \text{OH}$	1.50E07	2.0	7,547
B. Inhibited			
5. $\text{Cl}_2 + \text{M} \rightarrow 2\text{Cl} + \text{M}$	1.00E14	0	48,180
6. $\text{HCl} + \text{H} \rightarrow \text{H}_2 + \text{Cl}$	7.94E12	0	3,400
7. $\text{H} + \text{Cl}_2 \rightarrow \text{HCl} + \text{Cl}$	8.51E13	0	1,170

A. Without HCl:

$$\text{CO: 20\%, O}_2\text{: 10\% H}_2\text{: 1\%, N}_2\text{: 69\%}$$

B. With HCl:

$$\text{CO: 20\%, O}_2\text{: 10\%, H}_2\text{: 1\%, N}_2\text{: 67\%, HCl: 2\%}$$

The combustion takes place at 1000 K and 1 atm and the initial hydrogen radical mole fraction is 10^{-7} . Treat the flame as a batch reactor.

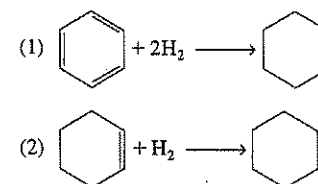
(a) Plot the mole fraction of each species and free radicals as a function of time for both uninhibited and inhibited combustions.

(b) Repeat part (a) for different temperatures and pressures.

(S. Senkan, UCLA)

P6-22_B The production of acetylene is described by R. W. Wansbaugh [Chem. Eng., 92(16), 95 (1985)]. Using the reaction and data in this article, develop a problem and solution.

P6-23_B The hydrogenation of benzene (B) is carried out in a CSTR slurry reactor where the desired product is cyclohexene (C) [Chem. Eng. Sci., 51, 2873 (1996)].



The rate laws for reactions (1) and (2) at 403 K are

$$\begin{aligned} -r_{1B} &= \frac{k_1 K_1 P_{\text{C}_6\text{H}_6} P_{\text{H}_2}^{1/2}}{1 + K_1 P_{\text{C}_6\text{H}_6}} & K_1 &= 0.0264 \text{ kPa}^{-1} \\ & & k_1 &= 2.7 \frac{\text{mol}}{\text{h} \cdot \text{kg} \cdot \text{cat} \cdot \text{kPa}^{0.5}} \\ -r_{2C} &= \frac{k_2 K_2 P_{\text{C}_6\text{H}_{10}} P_{\text{H}_2}}{1 + K_2 P_{\text{C}_6\text{H}_{10}}} & K_2 &= 0.04 \text{ kPa}^{-1} \\ & & k_2 &= 0.07 \frac{\text{mol}}{\text{h} \cdot \text{kg} \cdot \text{cat} \cdot \text{kPa}} \end{aligned}$$

with

$$130 \text{ kPa} < P_{\text{H}_2} < 2 \text{ MPa}$$

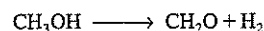
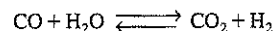
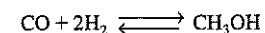
$$30 \text{ kPa} < P_{\text{C}_6\text{H}_6} < 450 \text{ MPa}$$

The entering molar flow rate of benzene is 2 mol/s and it is necessary to achieve at least 40% conversion of benzene at 403 K.

At what conditions should the reaction be carried out to maximize the yield of cyclohexene?

P6-24_C (Methanol synthesis) A new catalyst has been proposed for the synthesis of methanol from carbon monoxide and hydrogen gas. This catalyst is reason-

ably active between temperatures of 330 K to about 430 K. The isothermal reactions involved in the synthesis include



The reactions are elementary and take place in the gas phase. The reaction is to be carried out isothermally and as a first approximating pressure drop will be neglected. The feed consists of $\frac{7}{15}$ hydrogen gas, $\frac{1}{5}$ carbon monoxide, $\frac{1}{5}$ carbon dioxide, and $\frac{2}{15}$ steam. The total molar flow rate is 300 mol/s. The entering pressure may be varied between 1 atm and 160 atm and the entering temperature between 300 K and 400 K. Tubular (PFR) reactor volumes between 0.1 m³ and 2 m³ are available for use.

- (a) Determine the entering conditions of temperature and pressure and reactor volume that will optimize the production of methanol. (Hint: First try $T_o = 330$ at $P_o = 40$ atm, then try $T_o = 380$ $P_o = 1$ atm.)
- (b) Vary the ratios of the entering reactants to CO (i.e., Θ_{H_2} and $\Theta_{\text{H}_2\text{O}}$) to maximize methanol production. How do your results compare with those in part (a)? Describe what you find.

Additional information:

$$V = 40 \text{ dm}^3, T \text{ is in kelvin. } R = 1.987 \text{ cal/mol}$$

$$K_1 = \frac{131,667}{\exp\left[\frac{-30,620}{R} \cdot \left(\frac{1}{T} - \frac{1}{298}\right)\right]} (0.001987T)^2 \left(\frac{\text{dm}^3}{\text{mol}}\right)^2$$

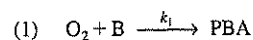
$$K_2 = \frac{103,943}{\exp\left[\frac{-9834}{R} \cdot \left(\frac{1}{T} - \frac{1}{298}\right)\right]}$$

$$k_1 = 0.933 \exp\left[2.5 \cdot \left(\frac{31,400}{R} \cdot \left(\frac{1}{330} - \frac{1}{T}\right)\right)\right] \left(\frac{\text{dm}^3}{\text{mol}}\right)^2 \text{ s}^{-1}$$

$$k_2 = 0.636 \exp\left[\frac{18,000}{R} \cdot \left(\frac{1}{300} - \frac{1}{T}\right)\right] \frac{\text{dm}^3}{\text{mol} \cdot \text{s}}$$

$$k_3 = 0.244 \exp\left[1.5 \cdot \left(\frac{28,956}{R} \cdot \left(\frac{1}{325} - \frac{1}{T}\right)\right)\right] \text{ s}^{-1}$$

- P6-25c** Oleic acid epoxide (E) is produced by the catalytic epoxidation of oleic acid (OA) [J. Fotopoulos, C. Georgakis, and H. Stenger, *Chem. Eng. Sci.*, 51, 1899 (1996)]. The raw materials are pure benzaldehyde (B) and oleic acid (OA). Unfortunately, undesired products are also formed, including benzoic (BA) and perbenzoic acids (PBA). The reaction sequence is



Additional information:

Concentration of pure B = 9.8 kmol/m³

Concentration of pure OA = 3.15 kmol/m³

Catalyst concentration = 4×10^{-5} kmol/m³

$$r_1 = \frac{k_1 [\text{cat}]^{0.5} [\text{B}]^{1.7}}{(1 + K_1 [\text{OA}])^{0.7}} \quad k_1 = 1.745 \left(\frac{\text{dm}^3}{\text{mol}}\right)^{1.2} \text{ min}^{-1} \text{ at } 47^\circ\text{C} \text{ with } E_1 = 18,500 \text{ cal/mol and } K_1 = 64.03 \text{ m}^3/\text{kmol}$$

$$r_2 = k_2 [\text{PBA}]^{0.5} [\text{OA}]^{0.6} \quad k_2 = 0.178 \left(\frac{\text{dm}^3}{\text{mol}}\right)^{0.1} \text{ min}^{-1} \text{ at } 47^\circ\text{C} \text{ with } E_2 = 9177 \text{ cal/mol}$$

$$r_3 = \frac{k_3 [\text{PBA}]^{1.0}}{(1 + K_3 [\text{OA}])^{1.0}} \quad k_3 = 0.08 \text{ min}^{-1} \text{ at } 47^\circ\text{C} \text{ with } E_3 = 17,132 \text{ cal/mol and } K_3 = 8.064 \text{ m}^3/\text{kmol}$$

How should the reaction be carried out (e.g. type of reactor(s), volume, temperature, feed rate) to produce 100 kmol of oleic acid epoxide (E) per day? There will be a prize for the solution that meets this criteria and minimizes the undesirable products. If equipment costs are available they should be included.

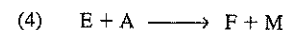
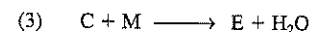
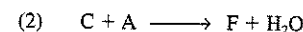
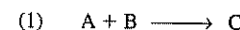
Additional information:

Concentration of pure oleic acid = 3.16 mol/dm³ = 3.16 kmol/m³

Concentration of pure benzaldehyde = 9.8 mol/dm³ = 9.8 kmol/m³

Typical catalyze concentration = 4×10^{-5} kmol/m³

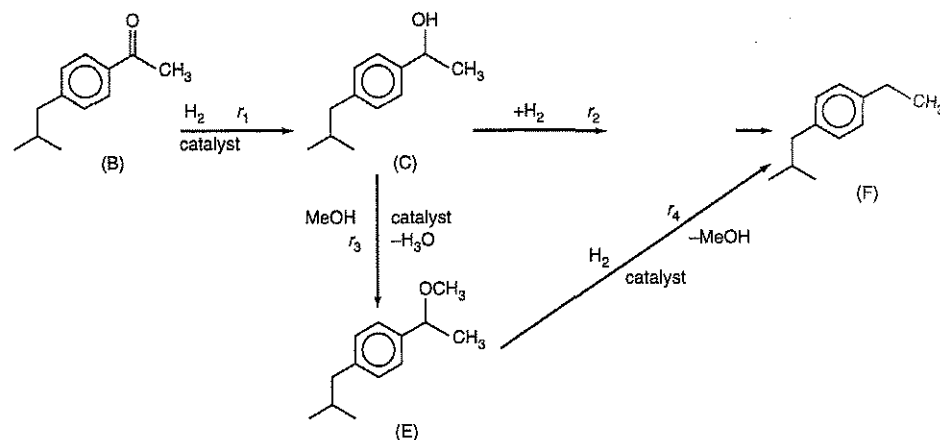
- P6-26c** A new catalytic pathway for an important intermediate in the production of the nonsteroidal anti-inflammatory drug ibuprofen (e.g., Advil) has been developed [*Chem. Eng. Sci.*, 51, 10, 1663 (1996)]. The pathway involves the hydrogenation of *p*-isobutyl acetophenone (B) in a solution of methanol containing a HY zeolite catalyst and saturated with hydrogen. The intermediate products are *p*-isobutylphenyl itanol (C), *p*-isobutylphenylethylmethyl ether (E) and *p*-isobutylethyl benzene (F). The reaction scheme is shown below. The following rate laws apply to the above equation.



$$-r_B = r_B = r_1 = \frac{wk_1 A^* B}{1 + k_A A^*} = \frac{wk_{1B} C_A C_B}{1 + K_A C_A} \quad (1)$$

$$-r_{2C} = r_2 = \frac{wk_2 A^* C}{1 + K_A A^*} = \frac{wk_{2C} C_A C_C}{1 + K_A C_A} \quad (2)$$





$$-r_{2C} = r_3 = wk_3C = wk_{2C}C_C \quad (3)$$

$$-r_{4E} = -r_4 = \frac{wk_4A^*E}{1 + k_4A^*} = \frac{wk_{4E}C_A C_E}{1 + K_A C_A} \quad (4)$$

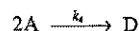
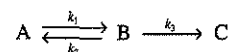
Because methanol, M, is in excess, it does not appear in the rate law. The rate and equilibrium constants are given in Table P6-26. The catalyst charge, w , is 10 kg/m³ and the initial concentration of *p*-isobutyl acetophenone, (B) is 0.54 kmol/dm³, the partial pressure of hydrogen is 5.9 MPa, and the temperature is 393 K. Plot the concentrations of A, B, C, D, E, and F as a function of time.

TABLE P6-26. RATE AND EQUILIBRIUM CONSTANTS

Temperature (K)	Rate parameters, [(m ³ /kg)(m ³ /kmol·s)] = $\frac{m^6}{kg \cdot kmol \cdot s}$					Henry's Law Constant $\frac{kmol}{m^3 \cdot MPa}$
	$k_1 \times 10^4$	$k_2 \times 10^4$	$k_3 \times 10^4$	$k_4 \times 10^4$	k_A (m ³ /kmol)	
373	3.2	1.5	9	7	26	0.055
393	4.68	2.27	28.2	14.7	22.76	0.058
413	8.5	4	95.2	30.4	18.03	0.061

* k_3 is in (m³/kg·s)

P6-27C For the van de Vusse elementary reactions



determine the reactor or combination of reactors that maximize the amount of B formed.

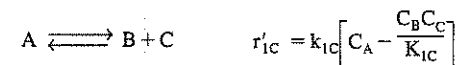
Additional information:

$$k_1 = 0.01 \text{ s}^{-1} \quad k_2 = 0.05 \text{ s}^{-1} \quad k_3 = 10 \text{ s}^{-1} \quad k_4 = 100 \text{ m}^3/\text{kmol}$$

$$C_{A0} = 2 \text{ kmol/m}^3 \text{ and } v_0 = 0.2 \text{ m}^3/\text{s}$$

Repeat for $k_2 = 0.002 \text{ s}^{-1}$.

P6-28B The gas phase reactions take place isothermally in a membrane reactor packed with catalyst. Pure A enters the reactor a 24.6 atm and 500K and a flow rate of A of 10 mol/min



Only species B diffuses out of the reactor through the membrane.

- Plot the concentrations down the length of the reactor.
- Explain why your curves look the way they do.
- Vary some of the parameters (e.g., k_B , k_{1C} , K_{1C}) and write a paragraph describing what you find.

Additional Information

Overall mass transfer coefficient $k_B = 1.0 \text{ dm}^3 / \text{kg cat} \cdot \text{min}$

$$k_{1C} = 2 \text{ dm}^3 / \text{kg cat} \cdot \text{min}$$

$$K_{1C} = 0.2 \text{ mol} / \text{dm}^3$$

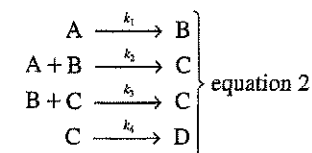
$$k_{2D} = 0.4 \text{ dm}^3 / \text{kg cat} \cdot \text{min}$$

$$k_{3E} = 5 \text{ dm}^3 / \text{mol}^2 \cdot \text{kg cat} \cdot \text{min}$$

$$W_f = 100 \text{ kg}$$

JOURNAL CRITIQUE PROBLEMS

- P6C-1** Is it possible to extrapolate the curves on Figure 2 [AIChE J., 17, 856 (1971)] to obtain the initial rate of reaction? Use the Wiesz-Prater criterion to determine if there are any diffusion limitations in this reaction. Determine the partial pressure of the products on the surface based on a selectivity for ethylene oxide ranging between 51 and 65% with conversions between 2.3 and 3.5%.
- P6C-2** Equation 5 [Chem. Eng. Sci., 35, 619 (1980)] is written to express the formation rate of C (olefins). As described in equation 2, there is no change in the concentration of C in the third reaction of the series:



- Determine if the rate law given in equation 5 is correct.
- Can equations 8, 9, and 12 be derived from equation 5?
- Is equation 14 correct?
- Are the adsorption coefficients b_i and b_j calculated correctly?

CD-ROM MATERIAL



• Learning Resources

1. Summary Notes for Lectures 11, 12, and 13

2. Web Modules

A. Cobra Bites

4. Solved Problems

A. CDP6-B_B All You Wanted to Know About Making Malic Anhydride and More.

5. Clarification: PFR with feed streams along the length of the reactor.

• Living Example Problems

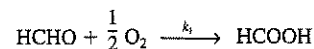
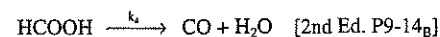
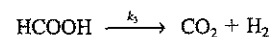
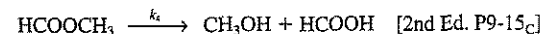
1. Example 6-6 Hydrodealkylation of Mesitylene in a PFR

2. Example 6-7 Hydrodealkylation of Mesitylene in a CSTR

3. Example 6-8 Calculating Concentrations as a Function of Position for NH₃ Oxidation in a PFR

• FAQ [Frequently Asked Questions]— In Updates/FAQ icon section

• Additional Homework Problems

CDP6-A_B Suggest a reaction system and conditions to minimize X and Y for the parallel reactions $A \longrightarrow X$, $A \longrightarrow B$, and $A \longrightarrow Y$. [2nd Ed. P9-5].CDP6-B_B Rework maleic anhydride problem, P6-14, for the case when reaction 1 is second order. [2nd Ed. P9-8]CDP6-C_B The reaction sequence $A \longrightarrow B$, $B \longrightarrow C$, $B \longrightarrow D$ is carried out in a batch reactor and in a CSTR. [2nd Ed. P9-12]CDP6-D_B Isobutylene is oxidized to methacroleum, CO, and CO₂. [1st Ed. P9-16]CDP6-E_B Given a batch reactor with $A \rightleftharpoons B \rightleftharpoons D$, calculate the composition after 6.5 h. [1st Ed. P9-11]CDP6-F_B Chlorination of benzene to monochlorobenzene and dichlorobenzene in a CSTR. [1st Ed. P9-14]CDP6-G_C Determine the number of independent reactions in the oxidation of ammonia. [1st Ed. P9-17]CDP6-H_B Oxidation of formaldehyde:CDP6-I_B Continuation of CDP6-H:CDP6-J_B Continuation of CDP6-H and I:CDP6-K_C Design a reactor for the alkylation of benzene with propylene to maximize the selectivity of isopropylbenzene. [Proc. 2nd Joint China/USA Chem. Eng. Conf. III, 51, (1997)].CDP6-L_D Reactions between paraffins and olefins to form highly branched paraffins are carried out in a slurry reactor to increase the octane number in gasoline. [Chem. Eng. Sci. 51, 10, 2053 (1996)].CDP6-M_A Design a reaction system to maximize the production of alkyl chloride. [1st Ed. P9-19]CDP6-N_C Design a reaction system to maximize the selectivity of *p*-xylene from methanol and toluene over a HZSM-8 zeolite catalyst. [2nd Ed. P9-17]CDP6-O_B Rework maleic anhydride problem, P6-14, for the case when reaction 1 is second order. [2nd Ed. P9-8]CDP6-P_C Oxidation of propylene to acrolein (Chem. Eng. Sci. 51, 2189 (1996)).

SUPPLEMENTARY READING

1. Selectivity, reactor schemes, and staging for multiple reactions, together with evaluation of the corresponding design equations, are presented in

DENBIGH, K. G., and J. C. R. TURNER, *Chemical Reactor Theory*, 2nd ed. Cambridge: Cambridge University Press, 1971, Chap. 6.LEVENSPIEL, O., *Chemical Reaction Engineering*, 2nd ed. New York: Wiley, 1972, Chap. 7.

Some example problems on reactor design for multiple reactions are presented in

HOUGEN, O. A., and K. M. WATSON, *Chemical Process Principles*, Part 3: *Kinetics and Catalysis*. New York: Wiley, 1947, Chap. XVIII.SMITH, J. M., *Chemical Engineering Kinetics*, 3rd ed. New York: McGraw-Hill, 1980, Chap. 4.

2. Books that have many analytical solutions for parallel, series, and combination reactions are

CAPELLOS, C., and B. H. J. BIELSKI, *Kinetic Systems*. New York: Wiley, 1972.WALAS, S. M., *Chemical Reaction Engineering Handbook of Solved Problems*. Newark, N.J.: Gordon and Breach, 1995.

3. A brief discussion of a number of pertinent references on parallel and series reactions is given in

ARIS, R., *Elementary Chemical Reactor Analysis*. Upper Saddle River, N.J.: Prentice Hall, 1969, Chap. 5.4. An excellent example of the determination of the specific reaction rates, k_i , in multiple reactions is given inBOUDART, M., and G. DIEGA-MARIADASSOU, *Kinetics of Heterogeneous Catalytic Reactions*. Princeton, N.J.: Princeton University Press, 1984.

Nonelementary Reaction Kinetics 7

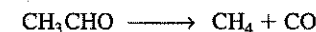
The next best thing to knowing something is knowing where to find it.

Samuel Johnson (1709–1784)

Until now, we have been discussing homogeneous reaction rate laws in which the concentration is raised to some power n , which is an integer. That is, the rate law (i.e., kinetic rate expression) is

$$-r_A = kC_A^n \quad (7-1)$$

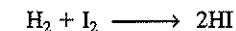
We said that if $n = 1$, the reaction was first-order with respect to A; if $n = 2$, the reaction was second-order with respect to A; and so on. However, a large number of homogeneous reactions involve the formation and subsequent reaction of an intermediate species. When this is the case it is not uncommon to find a reaction order that is not an integer. For example, the rate law for the decomposition of acetaldehyde,



at approximately 500°C is

$$-r_{\text{CH}_3\text{CHO}} = kC_{\text{CH}_3\text{CHO}}^{3/2} \quad (7-2)$$

Another common form of the rate law resulting from reactions involving active intermediates is one in which the rate is directly proportional to the reactant concentration and inversely proportional to the sum of a constant and the reactant concentration. An example of this type of kinetic expression is observed for the formation of hydrogen iodide,



The rate law for this reaction is

$$r_{HI} = \frac{k_1 k_3 C_{I_2} C_{H_2}}{k_2 + k_3 C_{H_2}} \quad (7-3)$$

For rate expressions similar or equivalent to those given by Equation (7-3), reaction orders cannot be defined. That is, for rate laws where the denominator is a polynomial function of the species concentrations, reaction orders are described only for limiting values of the reactant and/or product concentrations. Reactions of this type are nonelementary in that there is no direct correspondence between reaction order and stoichiometry.

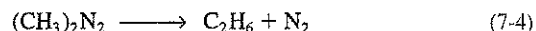
PSSH, Polymers,
Enzymes, Bacteria

In this chapter we discuss four topics: the pseudo-steady-state hypothesis, polymerization, enzymes, and bioreactors. The pseudo-steady-state hypothesis (PSSH) plays an important role in developing nonelementary rate laws. Consequently, we will first discuss the fundamentals of the PSSH, followed by its use of polymerization reactions and enzymatic reactions. Because enzymes are involved in all living organisms, we close the chapter with a discussion on bioreactions and reactors.

7.1 Fundamentals

Nonelementary rate laws similar to Equations (7-2) and (7-3) come about as a result of the overall reaction taking place by a mechanism consisting of a series of reaction steps. In our analysis, we assume each reaction step in the reaction mechanism to be *elementary*; the reaction orders and stoichiometric coefficients are identical.

To illustrate how rate laws of this type are formed, we shall first consider the gas-phase decomposition of azomethane, AZO, to give ethane and nitrogen:



Experimental observations show that the rate law for N_2 is first-order with respect to AZO at pressures greater than 1 atm (relatively high concentrations)

$$r_{\text{N}_2} \propto C_{\text{AZO}}$$

and second-order at pressures below 50 mmHg (low concentrations):¹

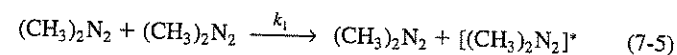
$$r_{\text{N}_2} \propto C_{\text{AZO}}^2$$

7.1.1 Active Intermediates

This apparent change in reaction order can be explained by the theory developed by Lindemann.² An activated molecule, $[(\text{CH}_3)_2\text{N}_2]^*$, results from collision or interaction between molecules:

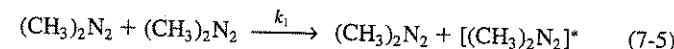
¹ H. C. Ramsperger, *J. Am. Chem. Soc.*, 49, 912 (1927).

² F. A. Lindemann, *Trans. Faraday Soc.*, 17, 598 (1922).



This activation can occur when translational kinetic energy is transferred into energy stored in internal degrees of freedom, particularly vibrational degrees of freedom.³ An unstable molecule (i.e., active intermediate) is not formed solely as a consequence of the molecule moving at a high velocity (high translational kinetic energy). The energy must be absorbed into the chemical bonds where high-amplitude oscillations will lead to bond ruptures, molecular rearrangement, and decomposition. In the absence of photochemical effects or similar phenomena, the transfer of translational energy to vibrational energy to produce an active intermediate can occur only as a consequence of molecular collision or interaction. Other types of active intermediates that can be formed are *free radicals* (one or more unpaired electrons, e.g., $\text{H}\cdot$), ionic intermediates (e.g., carbonium ion), and enzyme-substrate complexes, to mention a few.

In Lindemann's theory of active intermediates, decomposition of the intermediate does not occur instantaneously after internal activation of the molecule; rather, there is a time lag, although infinitesimally small, during which the species remains activated. For the azomethane reaction, the active intermediate is formed by the reaction



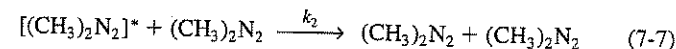
Because the reaction is elementary, the rate of formation of the active intermediate in Equation (7-5) is

$$r_{\text{AZO}^*(7-5)} = k_1 C_{\text{AZO}}^2 \quad (7-6)$$

where

$$\text{AZO} \equiv [(\text{CH}_3)_2\text{N}_2]$$

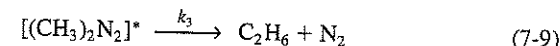
There are two reaction paths that the active intermediate (activated complex) may follow after being formed. In one path the activated molecule may become deactivated through collision with another molecule,



with

$$r_{\text{AZO}^*(7-7)} = -k_2 C_{\text{AZO}} C_{\text{AZO}^*} \quad (7-8)$$

This reaction is, of course, just the reverse reaction of that given by Equation (7-5). In the alternative path the active intermediate decomposes spontaneously to form ethane and nitrogen:



$$r_{\text{AZO}^*(7-9)} = -k_3 C_{\text{AZO}^*} \quad (7-10)$$

³ W. J. Moore, *Physical Chemistry*, 5th ed., Prentice Hall, Upper Saddle River, N.J., 1972.

Properties of an
active intermediate
A*

Nonelementary
reaction is seen as
a sequence of
elementary
reactions

The overall reaction [Equation (7-4)], for which the rate expression is nonelementary, consists of the sequence of elementary reactions, Equations (7-5), (7-7), and (7-9).

Nitrogen and ethane are only formed in the reaction given by Equation (7-9). Consequently, the net rate of formation of nitrogen is

$$r_{N_2} = k_3 C_{AZO^*} \quad (7-11)$$

Concentration of A^* is difficult to measure and needs to be replaced in the rate law

The concentration of the active intermediate, AZO^* , is very difficult to measure, because it is highly reactive and very short-lived ($\sim 10^{-9}$ s). Consequently, evaluation of the reaction rate laws, (7-8), (7-10), and (7-11), in their present forms becomes quite difficult, if not impossible. To overcome this difficulty, we need to express the concentration of the active intermediate, C_{AZO^*} , in terms of the concentration of azomethane, C_{AZO} . As mentioned in Chapter 3, the total or net rate of formation of a particular species involved in many simultaneous reactions is the sum of the rates of formation of each reaction for that species.

We can generalize the rate of formation of species j occurring in n different reactions as

The total rate of formation of species j from all reactions

$$r_j = \sum_{i=1}^n r_{ji} \quad (7-12)$$

Because the active intermediate, AZO^* , is present in all three reactions in the decomposition mechanism, the net rate of formation of AZO^* is the sum of the rates of each of the reaction equations, (7-5), (7-7), and (7-9):

$$\begin{bmatrix} \text{net rate of formation of } AZO^* \end{bmatrix} = \begin{bmatrix} \text{rate of formation of } AZO^* \text{ in Equation (7-5)} \end{bmatrix} + \begin{bmatrix} \text{rate of formation of } AZO^* \text{ in Equation (7-7)} \end{bmatrix} + \begin{bmatrix} \text{rate of formation of } AZO^* \text{ in Equation (7-9)} \end{bmatrix}$$

$$r_{AZO^*} = r_{AZO^*(7-5)} + r_{AZO^*(7-7)} + r_{AZO^*(7-9)} \quad (7-13)$$

By substituting Equations (7-6), (7-8), and (7-10) into Equation (7-13), we obtain

$$r_{AZO^*} = k_1 C_{AZO}^2 - k_2 C_{AZO} C_{AZO^*} - k_3 C_{AZO^*} \quad (7-14)$$

To express C_{AZO^*} in terms of measurable concentrations, we use the pseudo-steady-state hypothesis (PSSH).

7.1.2 Pseudo-Steady-State Hypothesis (PSSH)

In most instances it is not possible to eliminate the concentration of the active intermediate in the differential forms of the mole balance equations to obtain closed-form solutions. However, an approximate solution may be obtained. The active intermediate molecule has a very short lifetime because of

its high reactivity (i.e., large specific reaction rates). We shall also consider it to be present only in low concentrations. These two conditions lead to the pseudo-steady-state approximation, in which the rate of formation of the active intermediate is assumed to be equal to its rate of disappearance.⁴ As a result, the net rate of formation of the active intermediate, r^* , is zero:

$$r^* = 0$$

We found that the rate of formation of the product, nitrogen, was

$$r_{N_2} = k_3 C_{AZO^*} \quad (7-11)$$

and that the rate of formation of AZO^* was

$$r_{AZO^*} = k_1 C_{AZO}^2 - k_2 C_{AZO} C_{AZO^*} - k_3 C_{AZO^*} \quad (7-14)$$

Using the pseudo-steady-state hypothesis (PSSH), Equations (7-11) and (7-14) can be combined to obtain a rate law for N_2 solely in terms of the concentration of azomethane. First we solve for the concentration of the active intermediate AZO^* in terms of the concentration of azomethane, AZO . From the PSSH,

$$r_{AZO^*} = 0 \quad (7-15)$$

$$r_{AZO^*} = k_1 C_{AZO}^2 - k_2 C_{AZO} C_{AZO^*} - k_3 C_{AZO^*} = 0 \quad (7-16)$$

we can solve Equation (7-16) for C_{AZO^*} in terms of C_{AZO} :

$$C_{AZO^*} = \frac{k_1 C_{AZO}^2}{k_3 + k_2 C_{AZO}} \quad (7-17)$$

Substituting Equation (7-17) into Equation (7-11) gives

$$r_{N_2} = \frac{k_1 k_3 C_{AZO}^2}{k_3 + k_2 C_{AZO}} \quad (7-18)$$

At low concentrations

$$k_2 C_{AZO} \ll k_3$$

for which case we obtain the following second-order rate law:

$$r_{N_2} = k_1 C_{AZO}^2 \quad (7-19)$$

At high concentrations

$$k_2 C_{AZO} \gg k_3$$

The PSSH assumes that the net rate of formation of A^* is zero

The final form of the rate law

⁴For further elaboration on this section, see R. Aris, *Am. Sci.*, 58, 419 (1970).



Apparent reaction orders

in which case the rate expression follows first-order kinetics,

$$r_{N_2} = \frac{k_1 k_3}{k_2} C_{AZO} = k C_{AZO} \quad (7-20)$$

In describing reaction orders for this equation one would say the reaction is *apparent first-order* at high azomethane concentrations and *apparent second-order* at low azomethane concentrations.

7.2 Searching for a Mechanism

In many instances the rate data are correlated before a mechanism is found. It is a normal procedure to reduce the additive constant in the denominator to 1. We therefore divide the numerator and denominator of Equation (7-18) by k_3 to obtain

$$r_{N_2} = \frac{k_1 C_{AZO}^2}{1 + k' C_{AZO}} \quad (7-21)$$

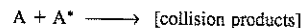
7.2.1 General Considerations

The rules of thumb listed in Table 7-1 may be of some help in the development of a mechanism that is consistent with the experimental rate law. Upon application of Table 7-1 to the azomethane example just discussed, we see from rate equation (7-18) that:

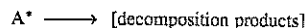
1. The active intermediate, AZO^* , collides with azomethane, AZO [Equation (7-7)], resulting in the appearance of the concentration of AZO in the denominator.
2. AZO^* decomposes spontaneously [Equation (7-9)], resulting in a constant in the denominator of the rate expression.
3. The appearance of AZO in the numerator suggests that the active intermediate AZO^* is formed from AZO . Referring to Equation (7-5), we see that this case is indeed true.

TABLE 7-1. RULES OF THUMB FOR DEVELOPMENT OF A MECHANISM

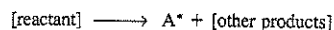
1. Species having the concentration(s) appearing in the denominator of the rate law probably collide with the active intermediate, e.g.,



2. If a constant appears in the denominator, one of the reaction steps is probably the spontaneous decomposition of the active intermediate, e.g.,

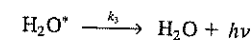


3. Species having the concentration(s) appearing in the numerator of the rate law probably produce the active intermediate in one of the reaction steps, e.g.,



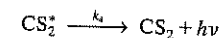
Example 7-1 The Stern-Volmer Equation

Light is given off when a high-intensity ultrasonic wave is applied to water.⁵ This light results from microsize bubbles being formed by the wave and then being compressed by it. During the compression stage of the wave, the contents of the bubble (e.g., water and whatever is dissolved in the water) are compressed adiabatically. This compression gives rise to high temperatures, which generate active intermediates and cause chemical reactions to occur in the bubble. The intensity of the light given off, I , is proportional to the rate of reaction of an activated water molecule that has been formed in the microbubble.



$$\text{intensity} \propto (-r_{H_2O^*}) = k_3 C_{H_2O^*}$$

An order-of-magnitude increase in the intensity of sonoluminescence is observed when either carbon disulfide or carbon tetrachloride is added to the water. The intensity of luminescence, I , for the reaction



is

$$I \propto (-r_{CS_2^*}) = k_4 C_{CS_2^*}$$

A similar result exists for CCl_4 .

However, when an aliphatic alcohol, X , is added to the solution, the intensity decreases with increasing concentration of alcohol. The data are usually reported in terms of a Stern-Volmer plot in which relative intensity is given as a function of alcohol concentration, C_X . (See Figure E7-1.1, where I_0 is the sonoluminescence intensity in the absence of alcohol and I is the sonoluminescence intensity in the presence of alcohol.) Suggest a mechanism consistent with experimental observation.

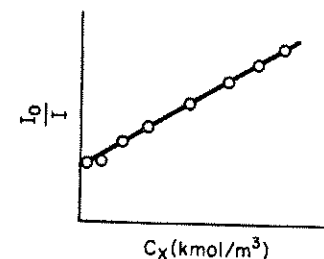


Figure E7-1.1

Stern-Volmer plot

⁵ P. K. Chendke and H. S. Fogler, *J. Phys. Chem.*, 87, 1362 (1983).

Solution

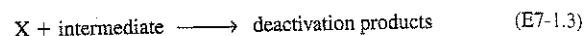
From the linear plot we know that

$$\frac{I_0}{I} = A + BC_X \equiv A + B(X) \quad (\text{E7-1.1})$$

where $C_X \equiv (X)$. Inverting yields

$$\frac{I}{I_0} = \frac{1}{A + B(X)} \quad (\text{E7-1.2})$$

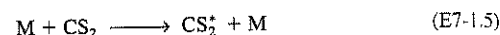
From rule 1 of Table 7-1, the denominator suggests that alcohol collides with the active intermediate:



The alcohol acts as what is called a scavenger to deactivate the active intermediate. The fact that the addition of CCl_4 or CS_2 increases the intensity of the luminescence,

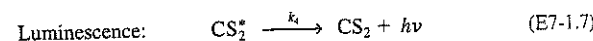
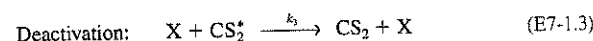
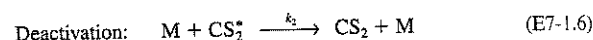
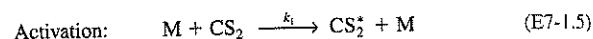
$$I \propto (\text{CS}_2) \quad (\text{E7-1.4})$$

leads us to postulate (rule 3 of Table 7-1) that the active intermediate was probably formed from CS_2 :



where M is a third body (CS_2 , H_2O , etc.).

We also know that deactivation can occur by the reverse of Reaction (E7-1.5). Combining this information, we have as our mechanism:



$$I = k_4(\text{CS}_2^*) \quad (\text{E7-1.8})$$

Using the PSSH on CS_2^* yields

$$r_{\text{CS}_2^*} = 0 = k_1(\text{CS}_2)(M) - k_2(\text{CS}_2^*)(M) - k_3(X)(\text{CS}_2^*) - k_4(\text{CS}_2^*)$$

Solving for CS_2^* and substituting into Equation (E7-1.8) gives us

$$I = \frac{k_4 k_1 (\text{CS}_2)(M)}{k_2(M) + k_3(X) + k_4} \quad (\text{E7-1.9})$$

In the absence of alcohol,

$$I_0 = \frac{k_4 k_1 (\text{CS}_2)(M)}{k_2(M) + k_4} \quad (\text{E7-1.10})$$

The mechanism

For constant concentrations of CS_2 and the third body, M , we take a ratio of Equation (E7-1.10) to (E7-1.9):

$$\frac{I_0}{I} = 1 + \frac{k_3}{k_2(M) + k_4}(X) = 1 + k'(X) \quad (\text{E7-1.11})$$

which is of the same form as that suggested by Figure E7-1.1. Equation (E7-1.11) and similar equations involving scavengers are called *Stern-Volmer equations*.

Now, let us proceed to some slightly more complex examples involving chain reactions. A chain reaction consists of the following sequence:

1. *Initiation*: formation of an active intermediate.
2. *Propagation or chain transfer*: interaction of an active intermediate with the reactant or product to produce another active intermediate.
3. *Termination*: deactivation of the active intermediate.

Steps in a chain reaction

Example 7-2 PSSH Applied to Thermal Cracking of Ethane

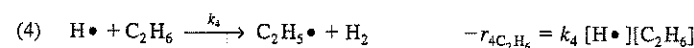
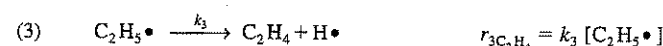
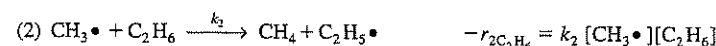
The thermal decomposition of ethane to ethylene, methane, butane, and hydrogen is believed to proceed in the following sequence:

Initiation:



$$\text{Let } k_1 = k_{\text{C}_2\text{H}_6}$$

Propagation:



Termination:



$$\text{Let } k_5 = k_{\text{C}_2\text{H}_5\cdot}$$

- (a) Use the PSSH to derive a rate law for the rate of formation of ethylene.
- (b) Compare the PSSH solution in Part (a) to that obtained by solving the complete set of ODE mole balances.

Solution

Part (a) Developing the Rate Law

The rate of formation of ethylene is

$$r_{\text{C}_2\text{H}_4} = k_3 [\text{C}_2\text{H}_5\cdot] \quad (\text{E7-2.1})$$

Given the following reaction sequence:

For the active intermediates: $\text{CH}_3\cdot$, $\text{C}_2\text{H}_5\cdot$, $\text{H}\cdot$ the net rates of reaction are

$$r_{\text{C}_2\text{H}_5\cdot} = r_{2\text{C}_2\text{H}_5\cdot} + r_{3\text{C}_2\text{H}_5\cdot} + r_{4\text{C}_2\text{H}_5\cdot} + r_{5\text{C}_2\text{H}_5\cdot} = 0$$

$$= -r_{2\text{C}_2\text{H}_6} - r_{3\text{C}_2\text{H}_4} - r_{4\text{C}_2\text{H}_6} + r_{5\text{C}_2\text{H}_5\cdot} = 0 \quad (\text{E7-2.2})$$

$$r_{\text{H}\cdot} = r_{3\text{C}_2\text{H}_4} + r_{4\text{C}_2\text{H}_6} = 0 \quad (\text{E7-2.3})$$

$$r_{\text{CH}_3\cdot} = -2r_{1\text{C}_2\text{H}_6} + r_{2\text{C}_2\text{H}_5\cdot} = 0 \quad (\text{E7-2.4})$$

Substituting the rate laws into Equation (E7-2.4) gives

$$2k_1[\text{C}_2\text{H}_6] - k_2[\text{CH}_3\cdot][\text{C}_2\text{H}_6] = 0 \quad (\text{E7-2.5})$$

$$[\text{CH}_3\cdot] = \frac{2k_1}{k_2} \quad (\text{E7-2.6})$$

Adding Equations (E7-2.2) and (E7-2.3) yields

$$-r_{2\text{C}_2\text{H}_6} + r_{5\text{C}_2\text{H}_5\cdot} = 0$$

$$k_2[\text{CH}_3\cdot][\text{C}_2\text{H}_6] - k_5[\text{C}_2\text{H}_5\cdot]^2 = 0 \quad (\text{E7-2.7})$$

Solving for $[\text{C}_2\text{H}_5\cdot]$ gives us

$$[\text{C}_2\text{H}_5\cdot] = \left\{ \frac{k_2}{k_5} [\text{CH}_3\cdot][\text{C}_2\text{H}_6] \right\}^{1/2} = \left\{ \frac{2k_1k_2}{k_2k_5} [\text{C}_2\text{H}_6] \right\}^{1/2}$$

$$= \left\{ \frac{2k_1}{k_5} [\text{C}_2\text{H}_6] \right\}^{1/2} \quad (\text{E7-2.8})$$

Substituting for $\text{C}_2\text{H}_5\cdot$ in Equation (E7-2.1) yields

$$r_{\text{C}_2\text{H}_4} = k_3[\text{C}_2\text{H}_5\cdot] = k_3 \left(\frac{2k_1}{k_5} \right)^{1/2} [\text{C}_2\text{H}_6]^{1/2} \quad (\text{E7-2.9})$$

$$r_{\text{C}_2\text{H}_6} = -k_1[\text{C}_2\text{H}_6] - k_2[\text{CH}_3\cdot][\text{C}_2\text{H}_6] - k_4[\text{H}\cdot][\text{C}_2\text{H}_6] \quad (\text{E7-2.10})$$

Substituting the rate laws in Equation (E7-2.3), we find that

$$k_3[\text{C}_2\text{H}_5\cdot] - k_4[\text{H}\cdot][\text{C}_2\text{H}_6] = 0$$

Using Equation (E7-2.8) to substitute for $\text{C}_2\text{H}_5\cdot$ gives

$$[\text{H}\cdot] = \frac{k_3}{k_4} \left(\frac{2k_1}{k_5} \right)^{1/2} [\text{C}_2\text{H}_6]^{-1/2} \quad (\text{E7-2.11})$$

The rate of disappearance of ethane now becomes

$$-r_{\text{C}_2\text{H}_6} = (k_1 + 2k_1)(\text{C}_2\text{H}_6) + k_3 \left(\frac{2k_1}{k_5} \right)^{1/2} \text{C}_2\text{H}_6^{1/2} \quad (\text{E7-2.12})$$

For a constant-volume batch reactor, the combined mole balances and rate laws for disappearance of ethane (P1) and the formation of ethylene (P5) are

$$\frac{dC_{P1}}{dt} = - \left[(3k_1C_{P1}) + k_3 \left(\frac{2k_1}{k_5} \right)^{1/2} C_{P1}^{1/2} \right] \quad (\text{E7-2.13})$$

$$\frac{dC_{P5}}{dt} = k_3 \left(\frac{2k_1}{k_5} \right)^{1/2} C_{P1}^{1/2} \quad (\text{E7-2.14})$$

The P in $P1$ (i.e., C_{P1}) and $P5$ (i.e., C_{P5}) is to remind us that we have used the PSSH in arriving at these balances.

At 1000 K the specific reaction rates are $k_1 = 1.5 \times 10^{-3} \text{ s}^{-1}$, $k_2 = 2.3 \times 10^6 \text{ dm}^3/\text{mol}\cdot\text{s}$, $k_3 = 5.71 \times 10^4 \text{ s}^{-1}$, $k_4 = 9.53 \times 10^8 \text{ dm}^3/\text{mol}\cdot\text{s}$, and $k_5 = 3.98 \times 10^9 \text{ dm}^3/\text{mol}\cdot\text{s}$.

For an entering ethane concentration of 0.1 mol/dm^3 and a temperature of 1000 K, Equations (E7-2.13) and (E7-2.14) were solved and the concentrations of ethane, C_{P1} , and ethylene, C_{P5} , are shown as a function of time in Figures E7-2.1 and E7-2.2.

In developing the above concentration-time relationship, we used PSSH. However, we can now utilize the techniques described in Chapter 6 to solve the full set of equations for ethane cracking and then compare these results with the much simpler PSSH solutions.

Part (b) Testing the PSSH for Ethane Cracking

The thermal cracking of ethane is believed to occur by the reaction sequence given in Part (a). The specific reaction rates are given as a function of temperature:

$$k_1 = 10e^{(87,000/R)(1/1250 - 1/T)} \text{ s}^{-1} \quad k_2 = 8.45 \times 10^6 e^{(13,000/R)(1/1250 - 1/T)} \text{ dm}^3/\text{mol}\cdot\text{s}$$

$$k_3 = 3.2 \times 10^6 e^{(46,000/R)(1/1250 - 1/T)} \text{ s}^{-1} \quad k_4 = 2.53 \times 10^9 e^{(9700/R)(1/1250 - 1/T)} \text{ dm}^3/\text{mol}\cdot\text{s}$$

$$k_5 = 3.98 \times 10^9 \text{ dm}^3/\text{mol}\cdot\text{s} \quad E = 0$$

Part (b): Plot the concentrations of ethane and ethylene as a function of time and compare with the PSSH concentration-time measurements. The initial concentration of ethane is 0.1 mol/dm^3 and the temperature is 1000 K.

Solution Part (b)

Let 1 = C_2H_6 , 2 = $\text{CH}_3\cdot$, 3 = CH_4 , 4 = $\text{C}_2\text{H}_5\cdot$, 5 = C_2H_4 , 6 = $\text{H}\cdot$, 7 = H_2 , and 8 = C_4H_{10} . The combined mole balances and rate laws become

$$(\text{C}_2\text{H}_6): \frac{dC_1}{dt} = -k_1C_1 - k_2C_1C_2 - k_4C_1C_6 \quad (\text{E7-2.13})$$

$$(\text{CH}_3\cdot): \frac{dC_2}{dt} = 2k_1C_1 - k_2C_2C_1 \quad (\text{E7-2.14})$$

$$(\text{CH}_4): \frac{dC_3}{dt} = k_2C_1C_2 \quad (\text{E7-2.15})$$

$$(C_2H_5\bullet): \frac{dC_4}{dt} = k_2C_1C_2 - k_3C_4 + k_4C_1C_6 - k_5C_4^2 \quad (E7-2.16)$$

$$(C_2H_4): \frac{dC_5}{dt} = k_3C_4 \quad (E7-2.17)$$

$$(H\bullet): \frac{dC_6}{dt} = k_3C_4 - k_4C_1C_6 \quad (E7-2.18)$$

$$(H_2): \frac{dC_7}{dt} = k_4C_1C_6 \quad (E7-2.19)$$

$$(C_4H_{10}): \frac{dC_8}{dt} = \frac{1}{2} k_5C_4^2 \quad (E7-2.20)$$

The POLYMATH program is given in Table E7-2.1.

TABLE E7-2.1. POLYMATH PROGRAM

Equations:	Initial Values:
$d(C_1)/d(t) = -k_1C_1 - k_2C_1C_2 - k_4C_1C_6$	0.1
$d(C_2)/d(t) = 2k_1C_1 - k_2C_1C_2$	0
$d(C_3)/d(t) = k_3C_4 - k_4C_1C_6$	0
$d(C_4)/d(t) = k_2C_1C_2 - k_3C_4 + k_4C_1C_6 - k_5C_4^2$	0
$d(C_5)/d(t) = k_3C_4$	0
$d(C_6)/d(t) = k_3C_4 - k_4C_1C_6$	0
$d(C_7)/d(t) = k_4C_1C_6$	0
$d(C_8)/d(t) = \frac{1}{2} k_5C_4^2$	0
$d(CP5)/d(t) = k_3 \cdot (2k_1/k_5)^{0.5} \cdot C_1^{0.5} \cdot C_4$	0.1
$d(CP1)/d(t) = -k_1C_1 - 2k_1C_1 \cdot (k_3 \cdot (2k_1/k_5)^{0.5}) \cdot (CP1^{0.5})$	
$k_5 = 3980000000$	
$T = 1000$	
$k_1 = 10 \cdot \exp((87500/1.987) \cdot (1/1250 - 1/T))$	
$k_2 = 64500000 \cdot \exp((13000/1.987) \cdot (1/1250 - 1/T))$	
$k_4 = 2530000000 \cdot \exp((9700/1.987) \cdot (1/1250 - 1/T))$	
$k_3 = 3200000 \cdot \exp((40000/1.987) \cdot (1/1250 - 1/T))$	
$t_0 = 0, \quad t_f = 12$	

Figure E7-2.1 shows a comparison of the concentration-time trajectory for ethane calculated from the PSSH (CP1) with the ethane trajectory (C1) calculated from solving the mole balance Equations (E7-2.14) through (E7-2.20). Figure E7-2.2 shows a similar comparison for ethylene (CP5) and (C5). One notes that the curves are identical, indicating the validity of the PSSH under these conditions. Figure E7-2.3 shows a comparison the concentration-time trajectories for methane (C3) and butane (C8). Problem P7-2(a) explores the temperature for which the PSSH is valid for the cracking of ethane.

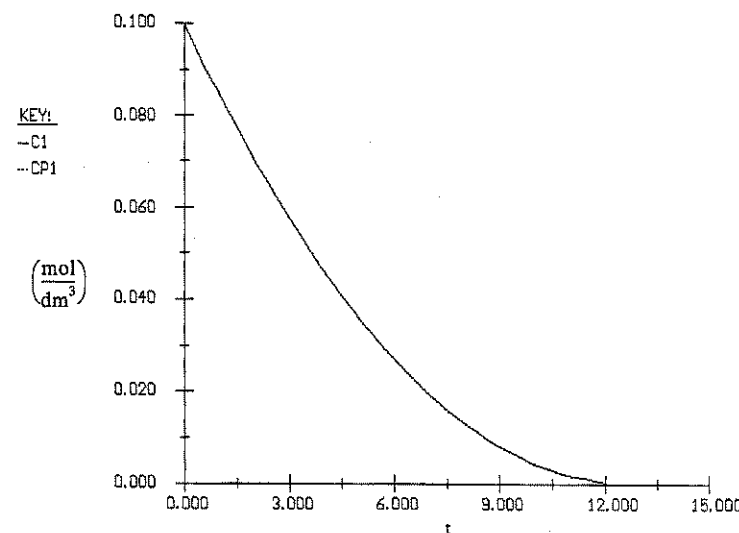
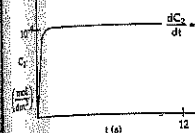


Figure E7-2.1 Comparison of concentration-time trajectories for ethane.

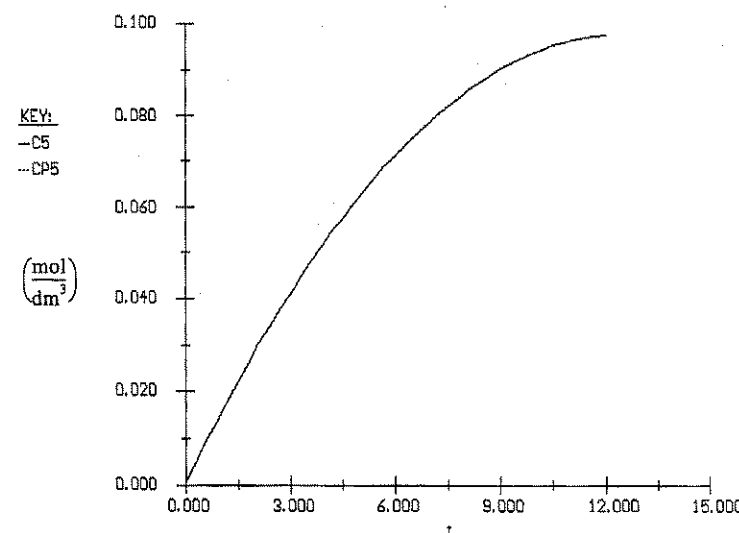


Figure E7-2.2 Comparison for temperature-time trajectory for ethylene.

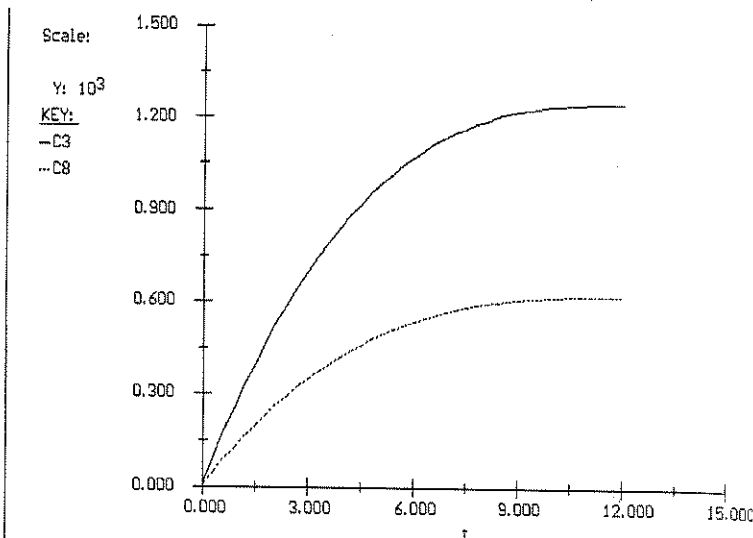


Figure E7-2.3 Comparison of concentration-time trajectories for methane (C3) and butane (C8).

7.2.2 Reaction Pathways

Ethane Cracking. With the increase in computing power, more and more analyses involving free-radical reactions as intermediates are carried out using the coupled sets of differential equations (cf. Example 7-2). The key in any such analyses is to identify which intermediate reactions are important in the overall sequence in predicting the end products. Once the key reactions are identified, one can sketch the pathways in a manner similar to that shown for the ethane cracking in Example 7-2 (see Figure 7-1).

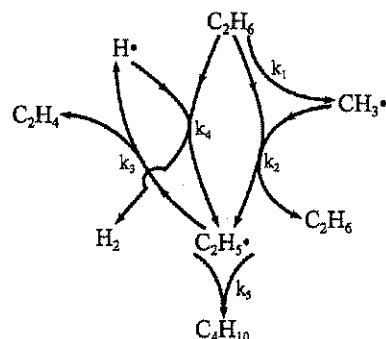
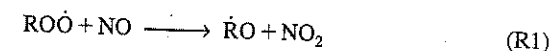
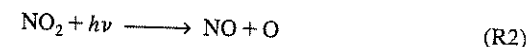


Figure 7-1 Pathway of ethane cracking.

Smog Formation. Nitrogen and oxygen react to form nitric oxide in the cylinder of automobile engines. The NO from automobile exhaust is oxidized to NO₂ in the presence of peroxide radicals.



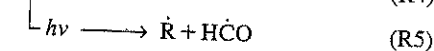
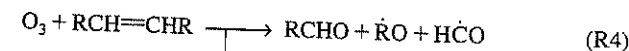
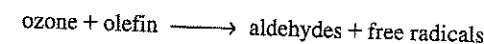
Nitrogen dioxide is then decomposed photochemically to give nascent oxygen,



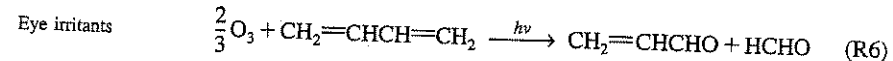
which reacts to form ozone:



The ozone then becomes involved in a whole series of reactions with hydrocarbons in the atmosphere to form aldehydes, various free radicals, and other intermediates, which react further to produce undesirable products in air pollution:



One specific example is the reaction of ozone with 1,3-butadiene to form acrolein and formaldehyde, which are *severe eye irritants*.



By regenerating NO₂, more ozone can be formed and the cycle continued. One means by which this regeneration may be accomplished is through the reaction of NO with the free radicals in the atmosphere (R1). For example, the free radical formed in Reaction (R4) can react with O₂ to give the peroxy free radical,



The coupling of all the reactions above is shown schematically in Figure 7-2.

We see that the cycle has been completed and that with a relatively small amount of nitrogen oxides, a large amount of pollutants can be produced. Of course, many other reactions are taking place, so do not be misled by the brevity of the preceding discussion; it does, however, serve to present, in rough outline, the role of nitrogen oxides in air pollution.

Finding the Reaction Mechanism. Now that a rate law has been synthesized from the experimental data, we shall try to propose a mechanism that is consistent with this equation. The method of attack will be as given in Table 7-2.

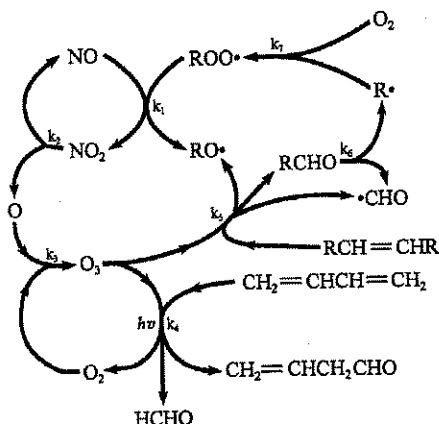


Figure 7-2 Reaction pathways in smog formation.

TABLE 7-2. STEPS TO DEDUCE A RATE LAW

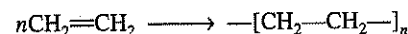
1. Assume an activated intermediate(s).
2. Postulate a mechanism, utilizing the rate law obtained from experimental data, if possible.
3. Model each reaction in the mechanism sequence as an elementary reaction.
4. After writing rate laws for the rate of formation of desired product, write the rate laws for each of the active intermediates.
5. Use the PSSH.
6. Eliminate the concentration of the intermediate species in the rate laws by solving the simultaneous equations developed in steps 4 and 5.
7. If the derived rate law does not agree with experimental observation, assume a new mechanism and/or intermediates and go to step 3. A strong background in organic and inorganic chemistry is helpful in predicting the activated intermediates for the reaction under consideration.

Once the rate law is found, the search for the mechanism begins

7.3 Polymerization

Polymers are finding increasing use throughout our society. Well over 100 billion pounds of polymer are produced each year and it is expected that this figure will double in the coming years as higher-strength plastics and composite materials replace metals in automobiles and other products. Consequently, the field of polymerization reaction engineering will have an even more prominent place in the chemical engineering profession. Since there are entire books on this field (see Supplementary Reading) it is the intention here to give only the most rudimentary thumbnail sketch of some of the principles of polymerization.

A polymer is a molecule made up of repeating structural (monomer) units. For example, polyethylene, which is used for such things as tubing, and electrical insulation is made up of repeating units of ethylene



where n may be 25,000 or higher.

Everyday Examples

Polyethylene
Softdrink cups
Sandwich bags
Poly (vinyl chloride)
Pipes
Shower curtains
Tygon tubing
Poly (vinyl acetate)
Chewing gum

Polymerization is the process in which monomer units are linked together by chemical reaction to form long chains. It is these long chains that set polymers apart from other chemical species and gives them their unique characteristic properties.

The polymer chains can be linear, branched, or cross-linked (Figure 7-3).

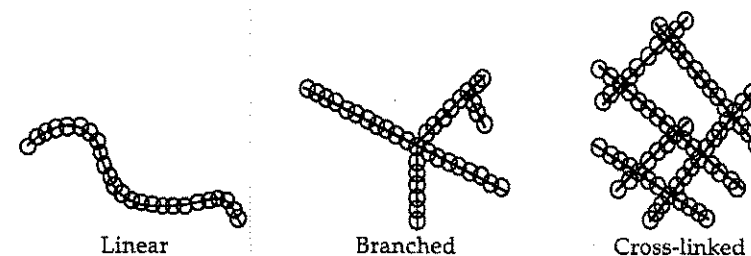
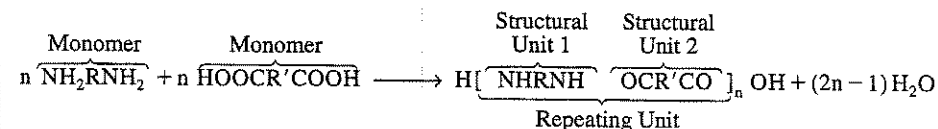


Figure 7-3 Types of polymer chains.

Homopolymers are polymers consisting of a single repeating unit, such as $[-CH_2-CH_2-]$. Homopolymers can also be made from two different monomers whose structural units form the repeating unit such as the formation of a polyamide (e.g., Nylon) from a diamine and a diacid.

Polymerization reactions are divided into two groups known as **step reactions** (also called condensation reactions) and **chain reactions**, also known as addition reactions. Step reactions require bifunctional or polyfunctional monomers, while chain reactions require the presence of an initiator.



Copolymers are polymers made up of two or more repeating units. There are five basic categories of copolymers that have two different repeating units Q and S. They are

- Categories
of Copolymers

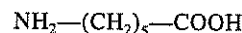
 1. *Alternating:* $\cdots Q-S-Q-S-Q-S-Q-S \cdots$
 2. *Block:* $\cdots Q-Q-Q-Q-S-S-S-S \cdots$
 3. *Random:* $\cdots Q-Q-Q-S-S-Q-S-S \cdots$
 4. *Graft:* $\begin{array}{c} \cdots Q-Q-Q-Q-Q-Q-Q-Q \cdots \\ | \\ S-S-S-S-S \end{array}$
 5. *Statistical* (follow certain addition laws)

Examples of each can be found in Young and Lovell.⁶

⁶ R. J. Young and P. A. Lovell, *Introduction to Polymers*, 2nd ed., Chapman & Hall, New York, 1991.

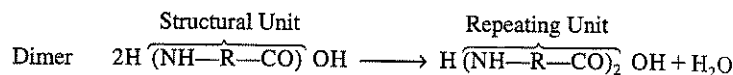
7.3.1 Step Polymerization

Step polymerization requires that there is at least a reactive functional group on each end of the monomer that will react with functional groups with other monomers. For example, amino-caproic acid



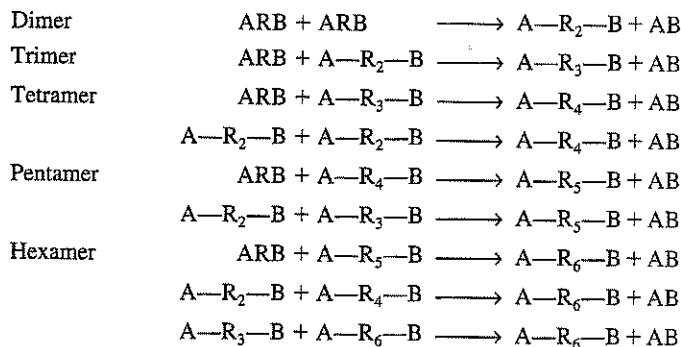
has an amine group at one end and a carboxyl group at the other. Some common functional groups are $-\text{OH}$, $-\text{COOH}$, $-\text{COCl}$, $-\text{NH}_2$.

In step polymerization the molecular weight usually builds up slowly

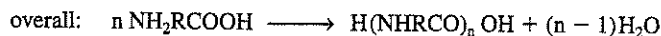


For the case shown above the structural unit and the repeating unit are the same.

Letting $\text{A} \equiv \text{H}$, $\text{R} \equiv \text{NH}-\text{R}_1-\text{CO}$, and $\text{B} \equiv \text{OH}$, $\text{AB} \equiv \text{H}_2\text{O}$. We can write the above reaction as

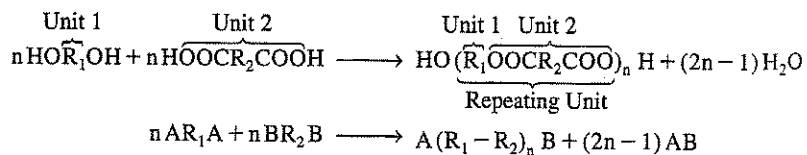


etc.



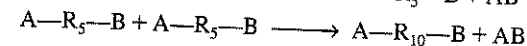
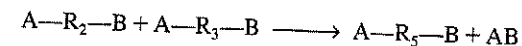
We see that from tetramers on, the n -mer can be formed by a number of different pathways.

The A and B functional groups can also be on different monomers such as the reaction for the formation of polyester (shirts) from diols and dibasic acids.



By using diols and diacids we can form polymers with two different structural units which together become the repeating unit. An example of an AR_1A plus BR_2B reaction is that used to make Coca-cola® bottles, i.e. terephthalic acid plus ethylene glycol to form poly (ethylene glycol terephthalate).

When discussing the progress of step polymerization it is not meaningful to use conversion of monomer as a measure because the reaction will still proceed even though all the monomer has been consumed. For example, if the monomer $\text{A}-\text{R}-\text{B}$ has been consumed. The polymerization is still continuing with



because there are both A and B functional groups that can react. Consequently, we measure the progress by the parameter p which is the fraction of functional groups, A, B, that have reacted. We shall only consider reaction with equal molar feed of functional groups. In this case

$$p = \frac{M_0 - M}{M_0} = \text{fraction of functional groups of either A or B that have reacted}$$

M = concentration of either A or B functional groups (mol/dm³)

As an example of step polymerization, consider the polyester reaction in which sulfuric acid is used as a catalyst in a batch reactor. Assuming the rate of disappearance is first order in A, B, and catalyst concentration (which is constant for an externally added catalyst). The balance on A is

$$\frac{-d[A]}{dt} = k[A][B] \quad (7-22)$$

For equal molar feed we have

$$[A] = [B] = M$$

$$\frac{dM}{dt} = -kM^2$$

$$M = \frac{M_0}{1 + M_0 kt} \quad (7-23)$$

In terms of the fractional conversion of functional groups, p ,

$$\frac{1}{1-p} = M_0 kt + 1 \quad (7-24)$$

The number average degree of polymerization, \bar{X}_n , is the average number of structural units per chain

$$\bar{X}_n = \frac{1}{1-p} \quad (7-25)$$

Degree
of Polymerization

The number average molecular weight, \bar{M}_n is just the average molecular weight of a structural unit \bar{M}_s , times the average number of structural unit per chain, \bar{X}_n plus the molecular weight of the end groups, M_{eg}

$$\bar{M}_n = \bar{X}_n \bar{M}_s + M_{eg}$$

Since M_{eg} is usually small (18 for the polyester reaction), it is neglected and

$$\bar{M}_n = \bar{X}_n \bar{M}_s \quad (7-26)$$

In addition to the conversion of the functional groups, the degree of polymerization, and the number average molecular weight we are interested in the distribution of chain lengths, n , (i.e. molecular weights M_n).

Example 7-3 Determining the concentrations of polymers for step polymerization

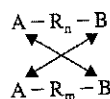
Determine the concentration and mole fraction of polymers of chain length j in terms of initial concentration of ARB, M_o , the concentration of unreacted functional groups M , the propagation constant k and time t .

Solution

Letting $P_1 = A-R-B$, $P_2 = A-R_2-B$, ... $P_j = A-R_j-B$ and omitting the water condensation products AB for each reaction we have

	Reaction	Rate Laws
(1)	$2P_1 \rightarrow P_2$	$-r_{1P_1} = 2kP_1^2, \quad r_{1P_2} = -\frac{r_{1P_1}}{2} = kP_1^2$
(2)	$P_1 + P_2 \rightarrow P_3$	$-r_{2P_1} = -r_{2P_2} = r_{2P_3} = 2kP_1P_2$
(3)	$P_1 + P_3 \rightarrow P_4$	$-r_{3P_1} = -r_{3P_3} = r_{3P_4} = 2kP_1P_3$
(4)	$P_2 + P_2 \rightarrow P_4$	$-r_{4P_2} = 2kP_2^2, \quad r_{4P_4} = -\frac{r_{4P_2}}{2} = kP_2^2$

The factor of 2 in the disappearance term (e.g. $-r_{3P_1} = 2kP_1P_3$) comes about because there are two ways A and B can react.



The net rate of reaction of P_1 , P_2 and P_3 for reactions (1) through (4) are

$$r_1 \equiv r_{P_1} = -2kP_1^2 - 2kP_1P_2 - 2kP_1P_3 \quad (E7-3.1)$$

$$r_2 \equiv r_{P_2} = kP_1^2 - 2kP_1P_2 - 2kP_2^2 \quad (E7-3.2)$$

$$r_3 \equiv r_{P_3} = 2kP_1P_2 - 2kP_1P_3 - 2kP_2P_3 \quad (E7-3.3)$$

If we continue in this way we would find that the net rate of formation of the P_1 is

$$r_{P_1} = -2kP_1 \sum_{j=1}^{\infty} P_j \quad (E7-3.4)$$

However, we note that $\sum_{j=1}^{\infty} P_j$ is just the total concentration of functional groups of

either A or B, which is $M \left(M = \sum_{j=1}^{\infty} P_j \right)$.

$$r_{P_1} = -2kP_1M \quad (E7-3.5)$$

Similarly we can generalize reactions (1) through (4) to obtain the net rate of formation of the j -mer, for $j \geq 2$.

$$r_j = k \sum_{i=1}^{j-1} P_i P_{j-i} - 2kP_jM \quad (E7-3.6)$$

For a batch reactor the mole balance on P_1 and using Equation (7-23) to eliminate M gives

$$\frac{dP_1}{dt} = -2kP_1M = -2kP_1 \frac{M_o}{1 + M_o kt} \quad (E7-3.7)$$

which solves to

$$P_1 = M_o \left(\frac{1}{1 + M_o kt} \right)^2 \quad (E7-3.8)$$

Having solved for P_1 we can now use r_j to solve successively for P_j

$$\frac{dP_2}{dt} = r_2 = kP_1^2 - 2kP_2M \quad (E7-3.9)$$

$$= kM_o^2 \left(\frac{1}{1 + M_o kt} \right)^4 - 2M_o k \left(\frac{1}{1 + M_o kt} \right) P_2 \quad (E7-3.10)$$

with $P_2 = 0$ at $t = 0$

$$P_2 = M_o \left(\frac{1}{1 + M_o kt} \right)^2 \left(\frac{M_o kt}{1 + M_o kt} \right) \quad (E7-3.11)$$

continuing we find, that in general⁷

$$P_j = M_o \left(\frac{1}{1 + M_o kt} \right)^2 \left(\frac{M_o kt}{1 + M_o kt} \right)^{j-1} \quad (E7-3.12)$$

⁷ N. A. Dotson, R. Galván, R. L. Lawrence, and M. Tirrell, *Polymerization Process Modeling*, VCH Publishers, New York, NY (1996).

$$\text{Recalling } p = \frac{M_o - M}{M_o}$$

$$P_j = M_o(1-p)^2 p^{j-1}$$

(E7-3.13)

The mole fraction of polymer with a chain length j is just

$$y_j = \frac{P_j}{M}$$

Recalling $M = M_o(1-p)$, we obtain

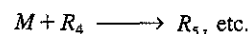
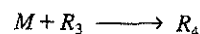
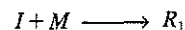
$$y_j = (1-p)p^{j-1}$$

(7-27)

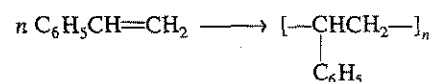
This is the Flory-Schulz distribution. We discuss this distribution further after we discuss chain reactions.

7.3.2 Chain Polymerizations Reactions

Chains (i.e., addition) polymerization requires an initiator (I) and proceeds by adding one repeating unit at a time.



Here the molecular weight in a chain usually builds up rapidly once a chain is initiated. The formation of polystyrene,



is an example of chain polymerization. A batch process to produce polystyrene for use in a number of molded objects is shown in Figure 7-4.

We can easily extend the concepts described in the preceding section to polymerization reactions. In this section we show how the rate laws are formulated so that one can use the techniques developed in Chapter 6 for multiple reactions to determine the molecular weight distribution and other properties. In the material that follows we focus on *free-radical polymerization*.

7.3.2.1 Steps in Free-Radical Polymerization

The basic steps in free-radical polymerization are initiation, propagation, chain transfer, and termination.

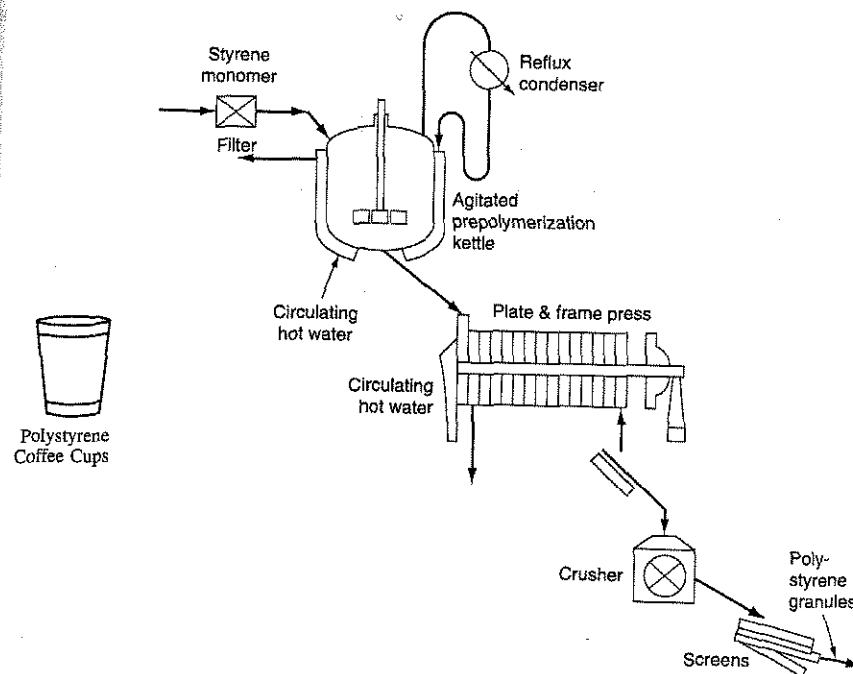
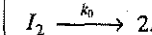


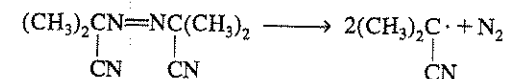
Figure 7-4 Batch bulk polystyrene process. (From *Chemical Reactor Theory*, p. 543, Copyright © 1977, Prentice Hall. Reprinted by permission of Prentice Hall, Upper Saddle River, NJ)

Initiation. Chain polymerization reactions are different because an initiation step is needed to start the polymer chain growth. Initiation can be achieved by adding a small amount of a chemical that decomposes easily to form free radicals. Initiators can be monofunctional and form the same free radical:

Initiation



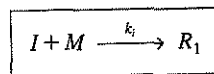
for example, 2,2-azobisisobutyronitrile:



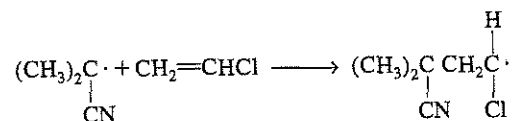
or they can be multifunctional and form different radicals. Multifunctional initiators contain more than one labile group⁸ [e.g., 2,5 dimethyl-2,5-bis(benzoylperoxy)hexane].

⁸ J. J. Kiu and K. Y. Choi, *Chem. Eng. Sci.*, 43, 65 (1988); K. Y. Choi and G. D. Lei, *AIChE J.*, 33, 2067 (1987).

For monofunctional initiators the reaction sequence between monomer M and initiator I is



for example,



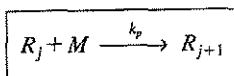
Propagation. The propagation sequence between a free radical R_1 with a monomer unit is



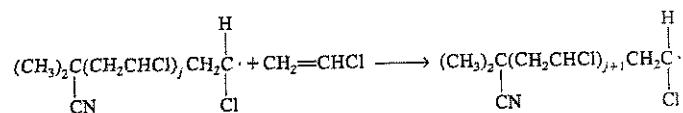
Propagation

In general,

Assumption of equal reactivity



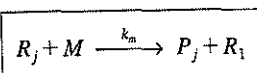
for example,



The specific reaction rates k_p are assumed to be identical for the addition of each monomer to the growing chain. This is usually an excellent assumption once two or more monomers have been added to R_1 and for low conversions of monomer. The specific reaction rate k_i is often taken to be equal to k_p .

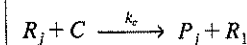
Chain Transfer. The transfer of a radical from a growing polymer chain can occur in the following ways:

1. Transfer to a monomer:

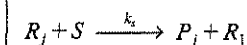


Here a *live* polymer chain of j monomer units transfers its free radical to the monomer to form the radical R_1 and a *dead* polymer chain of j monomer units.

2. Transfer to another species:



3. Transfer of the radical to the solvent:



The species involved in the various chain transfer reactions such as $\text{CCl}_3\cdot$ and $\text{C}_6\text{H}_5\text{CH}_2\cdot$ are all assumed to have the same reactivity as R_1 . In other words, all the R_1 's produced in chain transfer reactions are taken to be the same. However, in some cases the chain transfer agent may be too large or unreactive to propagate the chain. The choice of solvent in which to carry out the polymerization is important. For example, the solvent transfer specific reaction rate k_s is 10,000 times greater in CCl_4 than in benzene.

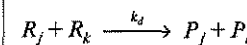
The specific reaction rates in chain transfer are all assumed to be independent of the chain length. We also note that while the radicals R_1 produced in each of the chain transfer steps are different, they function in essentially the same manner as the radical R_1 in the propagation step to form radical R_2 .

Termination. Termination to form dead polymer occurs primarily by two mechanisms:

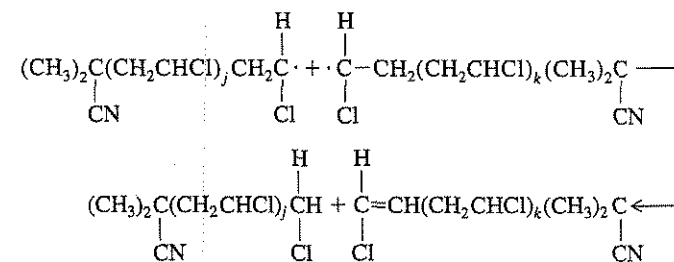
1. Addition (coupling) of two growing polymers:



2. Termination by disproportionation:



for example,



Termination



Chain transfer

The steps in free-radical polymerization reaction and the corresponding rate laws are summarized in Table 7-3. For the polymerization of styrene at 80°C initiated by 2,2-azobisisobutyronitrile the rate constants⁹ are

Initiation
Propagation
Transfer
Termination

$$\begin{aligned} k_0 &= 1.4 \times 10^{-3} \text{ s}^{-1} & k_m &= 3.2 \times 10^{-2} \text{ dm}^3/\text{mol} \cdot \text{s} \\ k_p &= 4.4 \times 10^2 \text{ dm}^3/\text{mol} \cdot \text{s} & k_a &= 1.2 \times 10^8 \text{ dm}^3/\text{mol} \cdot \text{s} \\ k_s &= 2.9 \times 10^{-3} \text{ dm}^3/\text{mol} \cdot \text{s} & k_d &= 0 \end{aligned}$$

TABLE 7-3

		Rate Law
Initiation:	$I_2 \xrightarrow{k_0} 2I$	$-r_{I_2} = k_0 I_2$
	$I + M \xrightarrow{k_i} R_1$	$r_{IJ} = 2fk_0 I_2$ $-r_i = k_i MI$
Propagation:	$R_j + M \xrightarrow{k_p} R_{j+1}$	$-r_j = k_p MR_j$
Chain transfer to: Monomer:	$R_j + M \xrightarrow{k_m} P_j + R_1$	$-r_{mj} = k_m MR_j$
Another species:	$R_j + C \xrightarrow{k_c} P_j + R_1$	$-r_{cj} = k_c CR_j$
Solvent:	$R_j + S \xrightarrow{k_s} P_j + R_1$	$-r_{sj} = k_s SR_j$
Termination: Addition:	$R_j + R_k \xrightarrow{k_a} P_{j+k}$	$-r_{aj} = k_a R_j R_k$
Disproportionation:	$R_j + R_k \xrightarrow{k_d} P_j + P_k$	$-r_{dj} = k_d R_j R_k$

Typical initial concentrations for the solution polymerization of styrene are 0.01 M for the initiator, 3 M for the monomer, and 7 M for the solvent.

7.3.2.2 Developing the Rate Laws for the Net Rate of Reaction

We begin by considering the rate of formation of the initiator radical I . Because there will always be scavenging or recombining of the primary radicals, only a certain fraction f will be successful in initiating polymer chains.

⁹ D. C. Timm and J. W. Rachow, *ACS Symposium Series 133*, H. M. Hulburt, ed., 1974, p. 122.

Since each reaction step is assumed to be elementary, the rate law for the formation of the initiator free radicals, r_{If} , is

$$r_{If} = 2fk_0(I_2)$$

where f is the fraction of initiator free radicals successful in initiating chaining and has a typical value in the range 0.2 to 0.7. The rate law for the formation of R_1 in the initiation step is

$$r_{R1} = -r_i = k_i(M)(I) \quad (7-28)$$

Using the PSSH for the initiator free radical, I , we have

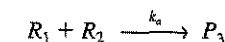
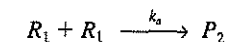
$$r_I = 2fk_0(I_2) - k_i(M)(I) = 0$$

$$(I) = \frac{2fk_0(I_2)}{(M)k_i} \quad (7-29)$$

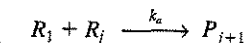
Then

$$-r_i = 2fk_0(I_2) \quad (7-30)$$

Before writing the rate of disappearance of R_1 , we need to make a couple of points. First, the radical R_1 can undergo the following termination sequence by addition.



Termination of R_1 In general,



Consequently, the total loss of R_1 radicals in the above reactions is found by adding the loss of R_1 radicals in each reaction so that the rate of disappearance by termination addition is given by

$$-r_{1t} = k_a R_1^2 + k_a R_1 R_2 + k_a R_1 R_3 + \cdots + k_a R_1 R_j + \cdots$$

$$-r_{1t} = k_a R_1 \sum_{j=1}^{\infty} R_j$$

Net rate of disappearance of radicals of chain length one

Free radicals usually have concentrations in the range 10^{-6} to 10^{-8} mol/dm³. We can now proceed to write the net rate of disappearance of the free radical, R_1 . [$R_1 \equiv (R_1) \equiv C_{R_1}$]

$$\begin{aligned} -r_1 = & -r_i + k_p R_1 M + k_a R_1 \sum_{j=1}^{\infty} R_j + k_d R_1 \sum_{j=1}^{\infty} R_j \\ & - k_m M \sum_{j=2}^{\infty} R_j - k_c C \sum_{j=2}^{\infty} R_j - k_s S \sum_{j=2}^{\infty} R_j \end{aligned} \quad (7-31)$$

Net rate of disappearance of radicals of chain length j

In general, the net rate of disappearance of live polymer chains with j monomer units (i.e., species j) for ($j \geq 2$) is

$$-r_j = k_p M(R_j - R_{j-1}) + (k_a + k_d) R_j \sum_{i=1}^{\infty} R_i + k_m M R_j + k_c C R_j + k_s S R_j \quad (7-32)$$

At this point one could use the techniques developed in Chapter 6 on multiple reactions to follow polymerization process. However, by using the PSSH, we can manipulate the rate law into a form that allows closed-form solutions for a number of polymerization reactions.

First, we let R^* be the total concentration of the radicals R_j :

$$R^* = \sum_{j=1}^{\infty} R_j \quad (7-33)$$

and k_t be the termination constant $k_t = (k_a + k_d)$. Next we sum Equation (7-32) over all free-radical chain lengths from $j = 2$ to $j = \infty$, and then add the result to Equation (7-31) to get

$$\sum_{j=1}^{\infty} -r_j = -r_i + k_t (R^*)^2$$

The total rate of termination is just

$$r_t = k_t (R^*)^2 \quad (7-34)$$

Using the PSSH for all free radicals, that is, $\sum_{j=1}^{\infty} -r_j = 0$, the total free-radical concentration solves to

$$R^* = \sqrt{\frac{-r_i}{k_t}} = \sqrt{\frac{2k_0(I_2)f}{k_t}} \quad (7-35)$$

Total free radical concentration

We now use this result in writing the net rate of monomer consumption. As a first approximation we will neglect the monomer consumed by monomer chain transfer. The net rate of monomer consumption, $-r_M$, is the rate of consumption by the initiator plus the rate of consumption by all the radicals R_j in each of the propagation steps (r_p).

$$-r_M = -r_i + -r_p = -r_i + k_p M \sum_{j=1}^{\infty} R_j$$

We now use the long-chain approximation (LCA). The LCA is that the rate of propagation is much greater than the rate of initiation:

$$\frac{r_p}{r_i} \gg 1$$

Long-chain approximation (LCA)

Substituting for r_p and r_i , we obtain

$$\begin{aligned} \frac{r_p}{r_i} &= \frac{-k_p M R^*}{-k_i M I} = \frac{k_p (2k_0 f(I_2)/k_i)^{1/2}}{k_i (2k_0 f(I_2)/M k_i)} \\ &= \frac{M}{I_2^{1/2}} \sqrt{\frac{k_p^2}{2k_0 f k_i}} \end{aligned}$$

Consequently, we see that the LCA is valid when both the ratio of monomer concentration to initiator concentration and the ratio of k_p^2 to $(k_0 f k_i)$ are high. Assuming the LCA gives

Rate of disappearance of monomer

$$-r_M = k_p M \sum_{j=1}^{\infty} R_j = k_p M R^* \quad (7-36)$$

Using Equation (7-35) to substitute for R^* , the rate of disappearance of monomer is

$$-r_M = k_p M \sqrt{\frac{2k_0(I_2)f}{k_t}} \quad (7-37)$$

The rate of disappearance of monomer, $-r_M$, is also equal to the rate of propagation, r_p :

$$r_p = -r_M$$

Finally, the net rate of formation of dead polymer P_j by addition is

$$r_{P_j} = 0.5 k_a \sum_{k=1}^{j-1} R_k R_{j-k} \quad (7-38)$$

The rate of formation of all dead polymers

$$\begin{aligned} r_P &= \sum_{j=1}^{\infty} r_{P_j} \\ r_P &= 0.5 k_a (R^*)^2 \end{aligned}$$

Rate of formation of dead polymers

7.3.3 Modeling a Batch Polymerization Reactor

To conclude this section we determine the concentration of monomer as a function of time in a batch reactor. A balance on the monomer combined with the LCA gives

$$\text{Monomer balance} \quad -\frac{dM}{dt} = k_p M \sum R_j = k_p M R^* = k_p M \sqrt{\frac{2k_0(I_2)f}{k_t}} \quad (7-39)$$

A balance on the initiator I_2 gives

$$\text{Initiator balance} \quad -\frac{dI_2}{dt} = k_0 I_2$$

Integrating and using the initial condition $I_2 = I_{20}$ at $t = 0$, we obtain the equation of the initiator concentration profile:

$$I_2 = I_{20} \exp(-k_0 t) \quad (7-40)$$

Substituting for the initiator concentration in Equation (7-39), we get

$$\frac{dM}{dt} = -k_p M \left(\frac{2k_0 I_{20} f}{k_t} \right)^{1/2} \exp\left(-\frac{k_0}{2} t\right) \quad (7-41)$$

Integration of Equation (7-41) gives

$$\ln \frac{M}{M_0} = \left(\frac{8k_p^2 f I_{20}}{k_0 k_t} \right)^{1/2} \left[\exp\left(-\frac{k_0 t}{2}\right) - 1 \right] \quad (7-42)$$

One notes that as $t \rightarrow \infty$, there will still be some monomer left unreacted. Why?

A plot of monomer concentration is shown as a function of time in Figure 7-5 for different initiator concentrations.

The fractional conversion of a monofunctional monomer is

$$X = \frac{M_0 - M}{M_0}$$

We see from Figure 7-5 that for an initiator concentration 0.001 M, the monomer concentration starts at 3 M and levels off at a concentration of 0.6 M, corresponding to a maximum conversion of 80%.

Now that we can determine the monomer concentration as a function of time, we will focus on determining the distribution of dead polymer, P_j . The concentrations of dead polymer and the molecular weight distribution can be derived in the following manner.¹⁰ The probability of propagation is

¹⁰E. J. Schork, P. B. Deshpande, K. W. Leffew, *Control of Polymerization Reactor*, New York: Marcel Dekker (1993).

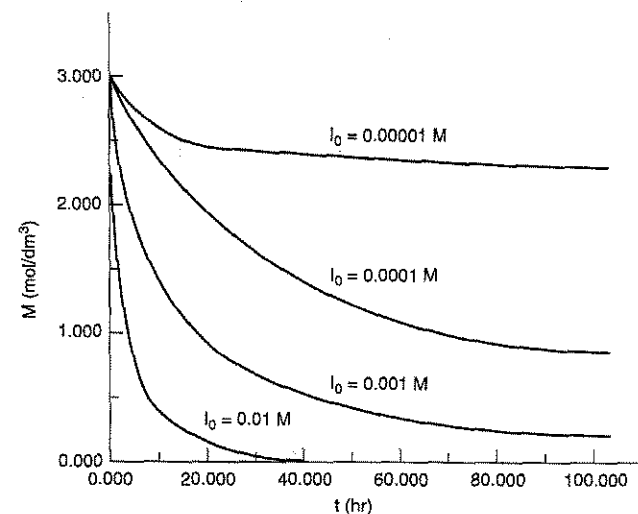


Figure 7-5 Monomer concentration as a functional time.

$$\beta = \frac{\text{rate of propagation}}{\text{rate of propagation} + \text{rate of termination}} = \frac{r_p}{r_p + r_t}$$

$$\beta = \frac{k_p M R^*}{k_p M R^* + k_s S R^* + k_m M R^* + k_c C R^* + k_t (R^*)^2}$$

Simplifying

$$\beta = \frac{k_p M}{k_p M + k_m M + k_c C + k_s S + \sqrt{2k_t k_0 f(I_2)}} \quad (7-43)$$

In the absence of chain transfer, the monomer concentration, M , can be determined from Equation (7-43) and concentration of initiator, I_2 , from Equation (7-40). Consequently we have β as a function of time.

It can be shown that in the absence of termination by combination, the mole fractions y_j and weight fraction w_j are exactly the same as those for step polymerization. That is if we set

$$\beta = p$$

we can determine the dead polymer concentrations and molecular weight distribution of dead polymer in free radical polymerization for the Flory distributions. For example, the concentration of dead polymer of chain length n is

$$P_n = y_n \left(\sum_{j=2}^{\infty} P_j \right) = \left(\sum_{j=2}^{\infty} P_j \right) (1-p) p^{n-1}$$

where $\left(\sum_{n=2}^{\infty} P_n\right)$ is the total dead polymer concentration and

$$y_n = (1-p)p^{n-1} \quad (7-27)$$

which is the same as the mole fraction obtained in step polymerization, i.e. Equation (7-27).

If the termination is only by disproportionation, the dead polymer P_j will have the same distribution as the live polymer R_j .

We will discuss the use of the Flory Equation after we discuss molecular weight distributions.

7.3.4 Molecular Weight Distribution

Although it is of interest to know the monomer concentration as a function of time (Figure 7-5), it is the polymer concentration, the average molecular weight, and the distribution of chain lengths that give a polymer its unique properties. Consequently, to obtain such things as the average chain length of the polymer, we need to determine the molecular weight distribution of radicals, (live polymer) R_j , and then dead polymers P_j as well as the molecular weight distribution. Consequently, we need to quantify these parameters. A typical distribution of chain lengths for all the P_j ($j = 1$ to $j = n$) is shown in Figure 7-6. Gel permeation chromatography is commonly used to determine the molecular weight distribution. We will now explore some properties of these distributions. If one divides the y-axis by the total concentration of polymer (i.e., $\sum P_j$), that axis simply becomes the mole fraction of polymer with j repeating units embedded in it (i.e., y_j).

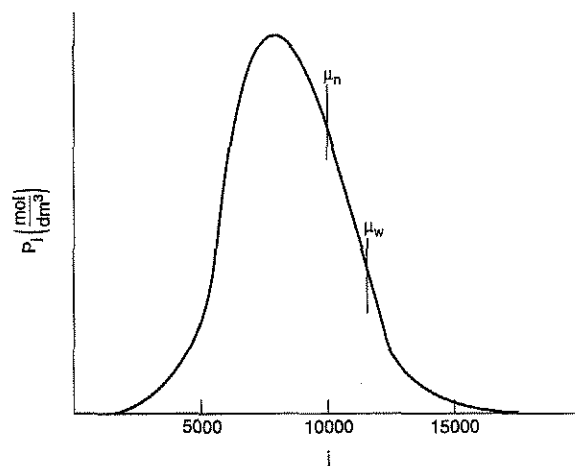


Figure 7-6 Distribution of concentration of dead polymers of length j .

Properties of the Distribution. From the distribution of molecular weights of polymers, some of the parameters one can use to quantify the distribution shown in Figure 7-6 and their relationships are given below.

1. The moments of the distribution

$$\lambda_n = \sum_{j=1}^{\infty} j^n P_j \quad (7-44)$$

2. The zeroth moment is just the total polymer concentration:

$$\lambda_0 = \sum_{j=1}^{\infty} P_j = P \quad (7-45)$$

3. The first moment is related to total number of monomer units (i.e., mass):

$$\lambda_1 = \sum_{j=1}^{\infty} j P_j \quad (7-46)$$

4. The first moment divided by the zeroth moment gives the *number-average chain length* (NACL), μ_n :

$$\text{NACL} = \mu_n = \frac{\lambda_1}{\lambda_0} = \frac{\sum j P_j}{\sum P_j} \quad (7-47)$$

For step-reaction polymerization, the NACL is also sometimes referred to as the *degree of polymerization*. It is the average number of structural units per chain and can also be calculated from

$$\mu_n = \bar{X}_n = \frac{1}{1-p}$$

5. The number-average molecular weight,

$$\bar{M}_n = \mu_n \bar{M}_s \quad (7-48)$$

where \bar{M}_s is the average molecular weight of the structural units. In chain polymerization, the average molecular weight of the structural unit is just the molecular weight of the monomer, M_M .

6. The second moment gives emphasis to the larger chains:

$$\lambda_2 = \sum_{j=1}^{\infty} j^2 P_j \quad (7-49)$$

7. The mass per unit volume of each polymer species is just $\bar{M}_s j P_j$. The mass average chain length is just the ratio of moment 2 to moment 1:

$$\text{WACL} = \frac{\lambda_2}{\lambda_1} = \mu_w = \frac{\sum j^2 P_j}{\sum j P_j} \quad (7-50)$$

8. The weight-average molecular weight is

$$\bar{M}_w = \bar{M}_s \mu_w \quad (7-51)$$

9. The number-average variance is

$$\sigma_n^2 = \frac{\lambda_2}{\lambda_0} - \left(\frac{\lambda_1}{\lambda_0} \right)^2 \quad (7-52)$$

10. The polydispersity index (D) is

$$D = \frac{\mu_w}{\mu_n} = \frac{\lambda_0 \lambda_2}{\lambda_1^2} \quad (7-53)$$

A polydispersity of 1 means that the polymers are all the same length and a polydispersity of 3 means that there is a wide distribution of polymer sizes. The polydispersity of typical polymers ranges from 2 to 10.

Example 7-4 Parameters Distributions of Polymers

A polymer was fractionated into the following six fractions:

Fraction	Molecular Weight	Mole Fraction
1	10,000	0.1
2	15,000	0.2
3	20,000	0.4
4	25,000	0.15
5	30,000	0.1
6	35,000	0.05

The molecular weight of the monomer was 25 Daltons.

Calculate NACL, WACL, the number variance, and the polydispersity.

Solution

MW	j	y	jy	j^2y
10,000	400	0.1	40	16,000
15,000	600	0.2	120	72,000
20,000	800	0.4	320	256,000
25,000	1000	0.15	150	150,000
30,000	1200	0.1	120	144,000
35,000	1400	0.05	70	98,000
			750	736,000

The number-average chain length, Equation (7-47), can be rearranged as

$$\begin{aligned} \text{NACL} &= \frac{\sum j P_j}{\sum P_j} = \sum j \frac{P_j}{\sum P_j} = \sum j y_j \\ &= \mu_n = 750 \text{ structural (monomer) units} \end{aligned} \quad (\text{E7-4.1})$$

The number-average molecular weight is

$$\bar{M}_n = \mu_n M = 750 \times 25 = 18,750$$

Recalling Equation (7-50) and rearranging, we have

$$\begin{aligned} \text{WACL} = \mu_w &= \frac{\sum j^2 P_j}{\sum j P_j} = \frac{\sum j^2 (P_j / \sum P_j)}{\sum j (P_j / \sum P_j)} \\ &= \frac{\sum j^2 y}{\sum j y} = \frac{736,000}{750} = 981.3 \text{ monomer units.} \end{aligned} \quad (\text{E7-4.2})$$

The mass average molecular weight is

$$\bar{M}_w = M_M \mu_w = 25 \times 981.33 = 24,533$$

The variance is

$$\begin{aligned} \sigma_n^2 &= \frac{\lambda_2}{\lambda_0} - \left(\frac{\lambda_1}{\lambda_0} \right)^2 = 736,000 - (750)^2 \\ &= 173,500 \\ \sigma_n &= 416 \end{aligned} \quad (\text{E7-4.3})$$

The polydispersity index D is

$$D = \frac{\bar{M}_w}{\bar{M}_n} = \frac{24,533}{18,750} = 1.31 \quad (\text{E7-4.4})$$

Flory Statistics of the Molecular Weight Distribution. The solution to the complete set ($j = 1$ to $j = 100,000$) of coupled-nonlinear ordinary differential equations needed to calculate the distribution is an enormous undertaking even with the fastest computers. However, we can use probability theory to estimate the distribution. This theory was developed by Nobel laureate Paul Flory. We have shown that for step polymerization and for free radical polymerization in which termination is by disproportionation the mole fraction of polymer with chain length j is

Flory mole fraction distribution

$$y_j = (1-p) p^{j-1} \quad (7-27)$$

In terms of the polymer concentration

$$P_j = y_j M = M_o (1-p)^2 p^{j-1} \quad (7-54)$$

The number average molecular weight

Termination other
than by combination

$$\begin{aligned}\bar{M}_n &= \sum_{j=1}^{\infty} y_j M_j = \sum_{j=1}^{\infty} y_j j \bar{M}_s \\ &= \bar{M}_s (1-p) \sum_{j=1}^{\infty} j p^{j-1} = \bar{M}_s (1-p) \frac{1}{(1-p)^2}\end{aligned}$$

and we see that the number average molecular weight is identical to that given by Equation (7-26)

$$\bar{M}_n = \bar{X}_n \bar{M}_s = \frac{\bar{M}_s}{1-p} \quad (7-26)$$

The weight fraction of polymer of chain length j is

$$\begin{aligned}w_j &= \frac{P_j M_j}{\sum_{j=1}^{\infty} P_j M_j} = \frac{P_j j \bar{M}_s}{\bar{M}_s \sum_{j=1}^{\infty} j P_j} = \frac{j P_j}{\sum_{j=1}^{\infty} j P_j} \\ &= \frac{j(1-p)^2 p^{j-1}}{(1-p)^2 \sum_{j=1}^{\infty} j p^{j-1}} \\ &= \frac{j(1-p)^2 p^{j-1}}{(1-p)^2 \frac{1}{(1-p)^2}} \\ &= j(1-p)^2 p^{j-1}\end{aligned} \quad (7-56)$$

Flory weight
fraction distribution

The weight fraction is shown in Figure 7-7 as a function of chain length.

The weight average molecular weight is

$$\bar{M}_w = \sum_{j=1}^{\infty} w_j M_j = \bar{M}_s \sum_{j=1}^{\infty} j w_j$$

$$\bar{M}_w = \bar{M}_s \frac{(1+p)}{(1-p)}$$

These equations will also apply for AR_1A and BR_2B polymers if the monomers are fed in stoichiometric portions. Equations (7-54) through (7-56) also can be used to obtain the distribution of concentration and molecular weights for radical reactions where termination is by chain transfer or by disproportionation if by p is given by Equation (7-43). However, they cannot be used for termination by combination.

Figure 7-7 compares the molecular weight distribution for poly(hexamethylene adipamide) calculated from Flory's most probable distribution¹¹ [Equa-

¹¹ P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, N.Y., 1953.

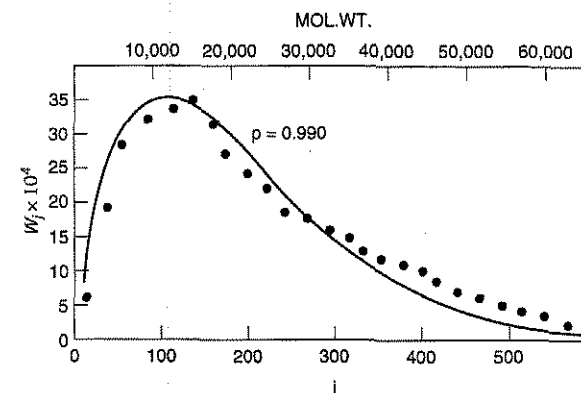


Figure 7-7 Molecular distribution. [Adapted from G. Tayler, *Journal of the American Chemical Society*, 69, p. 638, 1947. Reprinted by permission.]

tion (7-56)] for a conversion of 99% with the experimental values obtained by fractionation. One observes that the comparison is reasonably favorable.

For termination by combination, the mole fraction of polymers with j repeating units is

$$y_j = (j-1)(1-p)^2 p^{j-2} \quad (7-57)$$

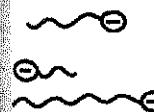
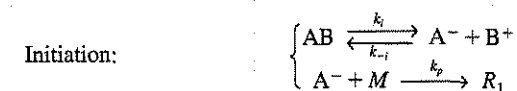
while the corresponding weight fraction is

$$w_j = \frac{1}{2} j(1-p)^3 (j-1) p^{j-2} \quad (7-58)$$

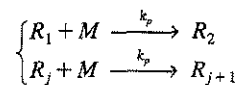
where p is given by Equation (7-43).

7.3.5 Anionic Polymerization

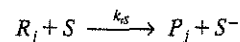
To illustrate the development of the growth of live polymer chains with time, we will use anionic polymerization. In anionic polymerization, initiation takes place by the addition of an anion, which is formed by dissociation of strong bases such as hydroxides, alkylolithium or alkoxides to which reacts with the monomer to form a active center, R_1^- . The dissociation of the initiator is very rapid and essentially at equilibrium. The propagation proceeds by the addition of monomer units to the end of the chain with the negative charge. Because the live ends of the polymer are negatively charged, termination can occur only by charge transfer to either the monomer or the solvent or by the addition of a neutralizing agent to the solution. Let $R_j^- \equiv R_j$ and the sequence of reactions for anionic polymerization becomes



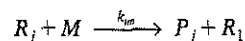
Propagation:



Chain transfer to solvent:



Transfer to monomer:



Batch reactor calculations

The corresponding combined batch reactor mole balances and rate laws are:
For the initiator:

$$\frac{dA^-}{dt} = k_i AB - k_{-i} A^- B^+ - k_p A^- M$$

For the live polymer:

$$\begin{aligned} \frac{dR_1}{dt} &= k_p A^- M - k_p R_1 M + k_{tm} M \sum_{j=1}^n R_j \\ \frac{dR_j}{dt} &= k_p (R_{j-1} - R_j) M - k_{ts} S R_j - k_{tm} M R_j \end{aligned}$$

For the dead polymer:

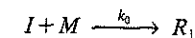
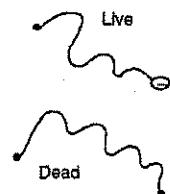
$$\frac{dP_j}{dt} = k_{ts} S R_j + k_{tm} M R_j$$

In theory one could solve this coupled set of differential equations. However, this process is very tedious and almost insurmountable if one were to carry it through for molecular weights of tens of thousands of Daltons, even with the fastest of computers. Fortunately, for some polymerization reactions there is a way out of this dilemma.

Some Approximations. To solve this set of coupled ODEs we need to make some approximations. There are a number of approximations that could be made, but we are going to make ones that allow us to obtain solutions that provide insight on how the live polymerization chains grow and dead polymer chains form. First we neglect the termination terms ($k_{ts} S R_j$ and $k_{tm} R_j M$) with respect to propagation terms in the mole balances. This assumption is an excellent one as long as the monomer concentration remains greater than the live polymer concentration.

For this point there are several assumptions that we can make. We could assume that the initiator ($I = A^-$) reacts slowly to form R_1 (such is the case in Problem P7-22).

"Houston, we have a problem!"
—Apollo 13



Initiation

$$\frac{dR_1}{dt} = k_0 MI - k_p R_1 M$$

Another assumption is that the rate of formation of R_1 from the initiator is instantaneous and that at time $t = 0$ the initial concentration of live polymer is $R_{10} = I_0$. This assumption is very reasonable for this initiation mechanism. Under the latter assumption the mole balances become

$$\text{Propagation} \quad \frac{dR_1}{dt} = -k_p M R_1 \quad (7-59)$$

$$\frac{dR_2}{dt} = k_p M (R_1 - R_2) \quad (7-60)$$

⋮

$$\frac{dR_j}{dt} = k_p (R_{j-1} - R_j) M \quad (7-61)$$

For the live polymer with the largest chain length that will exist, the mole balance is

$$\frac{dR_n}{dt} = k_p M R_{n-1} \quad (7-62)$$

If we sum Equations (7-59) through (7-62), we find that

$$\sum_{j=1}^n \frac{dR_j}{dt} = \frac{dR^*}{dt} = 0$$

Consequently, we see the total free live polymer concentration is a constant at $R^* = R_{10} = I_0$.

There are a number of different techniques that can be used to solve this set of equations, such as use of Laplace transforms, generating functions, statistical methods, and numerical and analytical techniques. We can obtain an analytical solution by using the following transformation. Let

$$d\Theta = k_p M dt \quad (7-63)$$

Then Equation (7-59) becomes

$$\frac{dR_1}{d\Theta} = -R_1 \quad (7-64)$$

Using the initial conditions that when $t = 0$, then $\Theta = 0$ and $R_1 = R_{10} = I_0$. Equation (7-64) solves to

$$R_1 = I_0 e^{-\Theta} \quad (7-65)$$

Next we transform Equation (7-60) to

$$\frac{dR_2}{d\Theta} = R_1 - R_2$$

and then substitute for R_1 :

$$\frac{dR_2}{d\Theta} + R_2 = I_0 e^{-\Theta}$$

With the aid of the integrating factor, e^Θ , along with the initial condition that at $t = 0$, $\Theta = 0$, $R_2 = 0$, we obtain

$$R_2 = I_0 (\Theta e^{-\Theta})$$

In a similar fashion,

$$R_3 = I_0 \left(\frac{\Theta^2}{2 \cdot 1} e^{-\Theta} \right)$$

$$R_4 = I_0 \left(\frac{\Theta^3}{3 \cdot 2 \cdot 1} e^{-\Theta} \right)$$

In general,

Concentration of
live polymer of
chain length j

$$R_j = I_0 \frac{\Theta^{j-1}}{(j-1)!} e^{-\Theta} \quad (7-66)$$

The live polymer concentrations are shown as a function of time and of chain length and time in Figures 7-8 and 7-9, respectively.

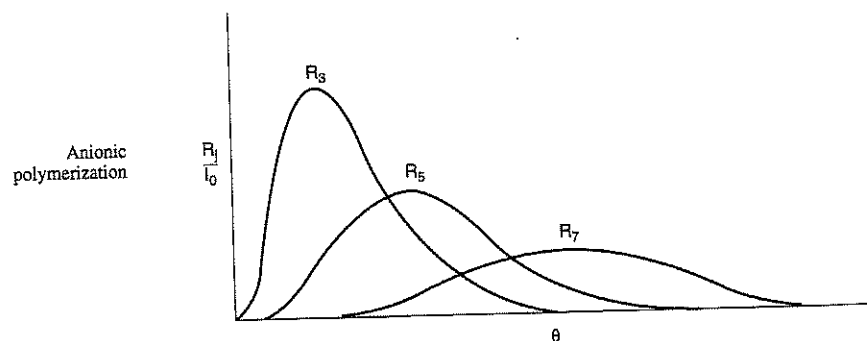


Figure 7-8 Live polymer concentration as a function of scaled time.

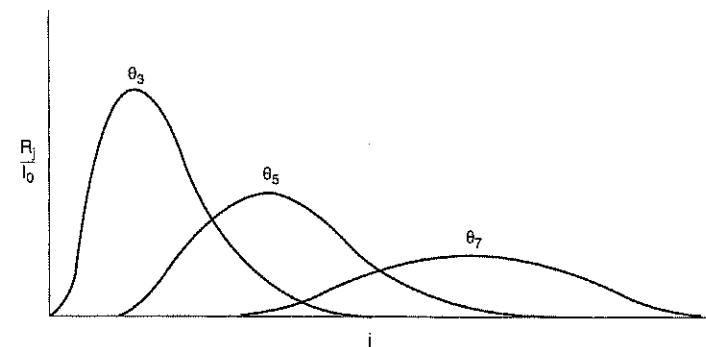


Figure 7-9 Live polymer concentration as a function of chain length at different scaled times.

Neglecting the rate of chain transfer to the monomer with respect to the rate of propagation, a mole balance on the monomer gives

$$\frac{dM}{dt} = -k_p M \sum_{j=1}^n R_j = -k_p M R_{10} = -k_p M I_0 \quad (7-67)$$

Knowing the initial monomer concentration, M_0 , we can solve for the monomer concentration at any time:

$$M = M_0 e^{-I_0 k_p t} \quad (7-68)$$

We can also evaluate the scaled time Θ :

$$\begin{aligned} \Theta &= \int_0^t k_p M dt = M_0 k_p \int_0^t e^{-I_0 k_p t} dt \\ &= + \frac{M_0 k_p}{k_p I_0} (e^{-I_0 k_p t}) \Big|_0^t \end{aligned}$$

$$\Theta = \frac{M_0}{I_0} (1 - e^{-I_0 k_p t}) \quad (7-69)$$

One can now substitute Equation (7-69) into Equation (7-66) to determine the live polymer concentrations at any time t .

For anionic polymerization, termination can occur by neutralizing the live polymer R_j to P_j .

Example 7-5 Calculating the Distribution Parameters from Analytical Expressions for Anionic Polymerization

Calculate μ_n , μ_m , and D for the live polymer chains R_j .

Solution

$$R_j = I_0 \frac{\Theta^{j-1}}{(j-1)!} e^{-\Theta} \quad (7-66)$$

We recall that the zero moment is just the total radical concentrations:

$$\lambda_0 = \sum_{j=1}^{\infty} R_j = I_0 \quad (E7-5.1)$$

The first moment is

$$\lambda_1 = \sum_{j=1}^{\infty} j R_j = I_0 \sum_{j=1}^{\infty} \frac{j \Theta^{j-1} e^{-\Theta}}{(j-1)!} \quad (E7-5.2)$$

Let $k = j - 1$:

$$\lambda_1 = I_0 \sum_{k=0}^{\infty} (k+1) \frac{\Theta^k e^{-\Theta}}{k!} \quad (E7-5.3)$$

Expanding the $(k+1)$ term gives

$$\lambda_1 = I_0 \left(\sum_{k=0}^{\infty} \frac{\Theta^k e^{-\Theta}}{k!} + \sum_{k=0}^{\infty} \frac{k \Theta^k e^{-\Theta}}{k!} \right) \quad (E7-5.4)$$

Recall that

$$\sum_{k=0}^{\infty} \frac{\Theta^k}{k!} = e^{\Theta} \quad (E7-5.5)$$

Therefore,

$$\lambda_1 = I_0 \left(1 + e^{-\Theta} \sum_{k=0}^{\infty} \frac{k \Theta^k}{k!} \right) \quad (E7-5.6)$$

Let $l = k - 1$:

$$\lambda_1 = I_0 \left(1 + e^{-\Theta} \Theta \sum_{l=0}^{\infty} \frac{\Theta^l}{l!} \right) = I_0 (1 + e^{-\Theta} \Theta e^{\Theta}) \quad (E7-5.7)$$

The first moment is

$$\lambda_1 = I_0 (1 + \Theta) \quad (E7-5.8)$$

The number-average length of growing polymer radical (i.e., live polymer) is

$$\mu_n = \frac{\lambda_1}{\lambda_0} = 1 + \Theta \quad (E7-5.9)$$

$$\lambda_2 = I_0 \sum_{j=0}^{\infty} j^2 R_j = I_0 \sum_{j=0}^{\infty} j^2 \frac{\Theta^{j-1}}{(j-1)!} \quad (E7-5.10)$$

Realizing that the $j = 0$ term in the summation is zero and after changing the index of the summation and some manipulation, we obtain

$$\lambda_2 = I_0 (1 + 3\Theta + \Theta^2) \quad (E7-5.11)$$

$$\mu_w = \frac{\lambda_2}{\lambda_1} = \frac{1 + 3\Theta + \Theta^2}{1 + \Theta} \quad (E7-5.12)$$

$$D = \frac{\mu_w}{\mu_n} = \frac{1 + 3\Theta + \Theta^2}{(1 + \Theta)^2} \quad (E7-5.13)$$

Plots of μ_n and μ_w along with the polydispersity, D , are shown in Figure E7-5.1.

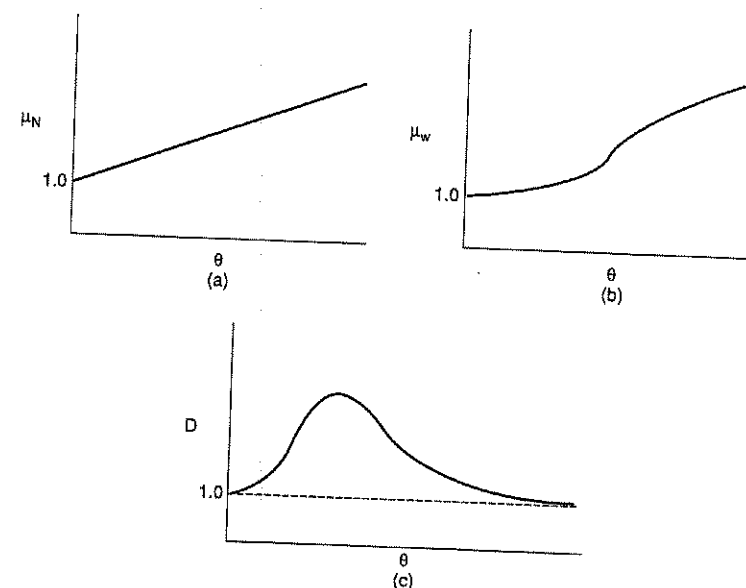


Figure E7-5.1 Moments of live polymer chain lengths: (a) number-average chain length; (b) weight-average chain length; (c) polydispersity.

We note from Equation (7-69) that after a long time the maximum value of Θ , Θ_M , will be reached:

$$\Theta_M = \frac{M_0}{I_0}$$

The distributions of live polymer species for an anionic polymerization carried out in a CSTR are developed in Problem P7-19.

Example 7-6 Determination of Dead Polymer Distribution When Transfer to Monomer Is the Main Termination Mechanism

Determine an equation for the concentration of polymer as a function of scaled time. Once we have the live polymer concentration as a function of time, we can determine the dead polymer concentration as a function of time. If transfer to monomer is the main mechanism for termination,



A balance of dead polymer of chain length j is

$$\frac{dP_j}{dt} = k_{tm} R_j M \quad (\text{E7-6.1})$$

As a *very* first approximation, we neglect the rate of transfer to dead polymer from the live polymer with respect to the rate of propagation:

$$(k_{tm} M R_j \ll k_p M R_j)$$

so that the analytical solution obtained in Equation (7-65) can be used. Then

$$\frac{dP_j}{d\Theta} = \frac{k_{tm}}{k_p} R_j = \frac{k_{tm}}{k_p} \frac{I_0 \Theta^{j-1} e^{-\Theta}}{(j-1)!} \quad (\text{E7-6.2})$$

Integrating, we obtain the dead polymer concentrations as a function of scaled time from CRC Mathematical Tables integral number 521:

$$P_j = \frac{k_{tm}}{k_p} I_0 \left[1 - e^{-\Theta} \left[\sum_{\ell=0}^{j-1} \frac{\Theta^{\ell} e^{-\Theta}}{\ell!} \right] \right] \quad (\text{E7-6.3})$$

We recall that the scaled time Θ can be calculated from

$$\Theta = \frac{M_0}{I_0} (1 - e^{-I_0 k_p t})$$

In many instances termination of anionic polymerization is brought about by adding a base to neutralize the propagating end of the polymer chain.

Other Useful Definitions. The number-average kinetic chain length, V_N , is the ratio of the rate of the propagation rate to the rate of termination:

$$V_N = \frac{r_p}{r_t} \quad (\text{7-70})$$

Most often, the PSSH is used so that $r_t = r_i$:

$$V_N = \frac{r_p}{r_i}$$

The long-chain approximation holds when V_N is large.

For the free-radical polymerization in which termination is by transfer to the monomer or a chain transfer agent and by addition, the kinetic chain length is

$$V_N = \frac{r_p}{r_t} = \frac{k_p M R^*}{k_{tm} M R^* + k_t (R^*)^2 + k_{ct} R^* C} = \frac{k_p M}{k_{tm} M + k_t R^* + k_{ct} C} \quad (\text{7-71})$$

$$V_N = \frac{k_p M}{k_{tm} M + (2k_t k_o I_2 f)^{1/2} + k_{ct} C}$$

For termination by combination

$$\bar{M}_n = 2V_N M_M$$

and for termination by disproportionation

$$\bar{M}_n = V_N M_M$$

Excellent examples that will reinforce and expand the principles discussed in this section can be found in Holland and Anthony,¹² and the reader is encouraged to consult this text as the next step in studying polymer reaction engineering.

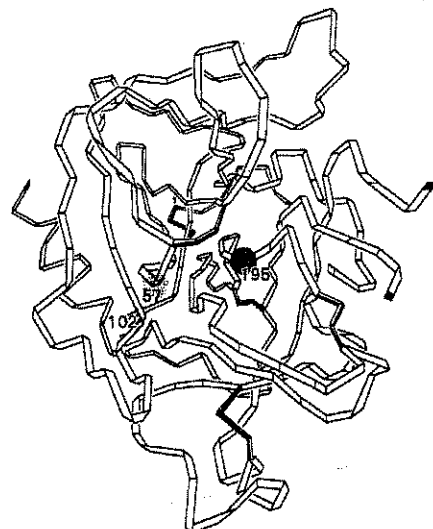
7.4 Enzymatic Reaction Fundamentals

7.4.1 Definitions and Mechanisms

Another class of reactions in which the PSSH is used is the enzymatically catalyzed reaction, which is characteristic of most biological reactions. An enzyme, E, is a protein or proteinlike substance with catalytic properties. A substrate, S, is the substance that is chemically transformed at an accelerated rate because of the action of the enzyme on it. An important property of enzymes is that they are specific in that *one* enzyme can catalyze only *one* reaction. For example, a protease hydrolyzes *only* bonds specific between specific amino acids in proteins, an amylase works on bonds between glucose molecules in starch, and lipase attacks fats, degrading them to fatty acids and glycerol. Consequently, unwanted products are easily controlled. Enzymes are produced only by living organisms, and commercial enzymes are generally produced by bacteria. Enzymes usually work (i.e., catalyze reactions) under mild conditions: pH 4 to 9 and temperatures 75 to 160°F.

Figure 7-10 shows the schematic of the enzyme chymotrypsin. In many cases the enzyme's active catalytic sites are found where the various loops interact. For chymotrypsin the catalytic sites are noted by the numbers 57, 102, and 195 in Figure 7-10. A number of structures of enzymes or pertinent information can be found on the following WWW sites:

¹²C. D. Holland and R. G. Anthony, *Fundamentals of Chemical Reaction Engineering*, 2nd ed., Prentice Hall, Upper Saddle River, N.J., 1977, p. 457.



Chymotrypsin

Figure 7-10 Enzyme urease. [From *Biochemistry*, 3/E by Stryer © 1988 by Lubert Stryer. Used with permission of W. H. Freeman and Company.]

<http://expasy.hcuge.ch/sprot/enzyme.html>

http://www.wcslc.edu/pers_pages/w-pool/chem350/chap6/

These sites also give information about enzymatic reactions in general.

Most enzymes are named in terms of the reactions they catalyze. It is a customary practice to add the suffix *-ase* to a major part of the name of the substrate on which the enzyme acts. For example, the enzyme that catalyzes the decomposition of urea is urease and the enzyme that attacks tyrosine is tyrosinase.

There are three major types of enzyme reactions:

Types of enzyme reactions

- I. Soluble enzyme–insoluble substrate
- II. Insoluble enzyme–soluble substrate
- III. Soluble enzyme–soluble substrate

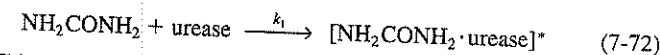
An example of a type I reaction is the use of enzymes such as proteases or amylases in laundry detergents; however, this enzyme reaction has caused some controversy in relation to water pollution. Once in solution, the soluble enzyme may digest (i.e., break down) an insoluble substrate such as a blood stain.

A major research effort is currently being directed at type II reactions. By attaching active enzyme groups to solid surfaces, continuous processing units similar to the packed catalytic bed reactor discussed in Chapter 10 can be developed.

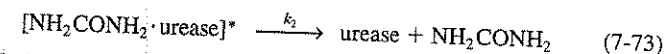
Clearly, the greatest activity in the study of enzymes has been in relation to biological reactions, because virtually every synthetic and degradation reaction in all living cells has been shown to be controlled and catalyzed by specific enzymes.¹³ Many of these reactions are homogeneous in the liquid phase; that is, they are type III reactions (soluble enzyme–soluble substrate). In the following brief presentation we limit our discussion to type III reactions, although the resulting equations have been found to be applicable to type I and type II reactions in certain instances.

In developing some of the elementary principles of the kinetics of enzyme reactions, we shall discuss an enzymatic reaction that has been suggested by Levine and LaCourse as part of a system that would reduce the size of an artificial kidney.¹⁴ The desired result is the production of an artificial kidney that could be worn by the patient and would incorporate a replaceable unit for the elimination of the nitrogenous waste products such as uric acid and creatinine. In the microencapsulation scheme proposed by Levine and LaCourse, the enzyme urease would be used in the removal of urea from the bloodstream. Here, the catalytic action of urease would cause urea to decompose into ammonia and carbon dioxide. The mechanism of the reaction is believed to proceed by the following sequence of elementary reactions:

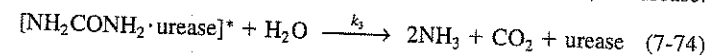
1. The enzyme urease reacts with the substrate urea to form an enzyme–substrate complex, $E \cdot S$:



2. This complex can decompose back to urea and urease:

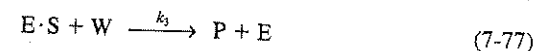
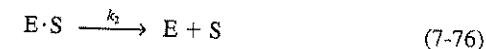


3. Or it can react with water to give ammonia, carbon dioxide, and urease:



We see that some of the enzyme added to the solution binds to the urea, and some remains unbound. Although we can easily measure the total concentration of enzyme, (E_t), it is difficult to measure the concentration of free enzyme, (E).

Letting E , S , W , $E \cdot S$, and P represent the enzyme, substrate, water, the enzyme–substrate complex, and the reaction products, respectively, we can write Reactions (7-72), (7-73), and (7-74) symbolically in the forms



Here $P = 2NH_3 + CO_2$.

¹³R. G. Denkwalter and R. Hirschmann, *Am. Sci.*, 57(4), 389 (1969).

¹⁴N. Levine and W. C. LaCourse, *J. Biomed. Mater. Res.*, 1, 275 (1967).

The reaction mechanism

We need to replace unbound enzyme concentration (E) in the rate law

The rate of disappearance of the substrate, $-r_s$, is

$$-r_s = k_1(E)(S) - k_2(E \cdot S) \quad (7-78)$$

The net rate of formation of the enzyme-substrate complex is

$$r_{E \cdot S} = k_1(E)(S) - k_2(E \cdot S) - k_3(W)(E \cdot S) \quad (7-79)$$

We note from the reaction sequence that the enzyme is not consumed by the reaction. The total concentration of the enzyme in the system, (E_t) , is constant and equal to the sum of the concentrations of the free or unbound enzyme E and the enzyme-substrate complex $E \cdot S$:

$$(E_t) = (E) + (E \cdot S) \quad (7-80)$$

Rearranging Equation (7-80), the enzyme concentration becomes

$$(E) = (E_t) - (E \cdot S) \quad (7-81)$$

Substituting Equation (7-81) into Equation (7-79) and using the PSSH for the enzyme complex gives

$$r_{E \cdot S} = 0 = k_1[(E_t) - (E \cdot S)](S) - k_2(E \cdot S) - k_3(E \cdot S)(W) \quad (7-82)$$

Solving for $(E \cdot S)$ yields

$$(E \cdot S) = \frac{k_1(E_t)(S)}{k_1(S) + k_2 + k_3(W)} \quad (7-83)$$

Next, substituting Equation (7-81) into Equation (7-78) yields

$$-r_s = k_1[(E_t) - (E \cdot S)](S) - k_2(E \cdot S) \quad (7-84)$$

Subtracting Equation (7-82) from Equation (7-84), we get

$$-r_s = k_3(W)(E \cdot S) \quad (7-85)$$

Substituting for $(E \cdot S)$ gives us

$$-r_s = \frac{k_1 k_3 (W) (E_t) (S)}{k_1 (S) + k_2 + k_3 (W)} \quad (7-86)$$

The final form of the rate law

Note: Throughout, $E_t \equiv (E_t)$ = total concentration of enzyme with typical units (kmol/m^3).

7.4.2 Michaelis-Menten Equation

Because the reaction of urea and urease is carried out in aqueous solution, water is, of course, in excess, and the concentration of water is therefore considered constant. Let

$$k'_3 = k_3(W) \quad \text{and} \quad K_m = \frac{k'_2 + k_3}{k_1}$$

Dividing the numerator and denominator of Equation (7-86) by k_1 , we obtain a form of the *Michaelis-Menten equation*:

$$-r_s = \frac{k'_3 (S) (E_t)}{(S) + K_m} \quad (7-87)$$

where K_m is called the Michaelis constant. If, in addition, we let V_{\max} represent the maximum rate of reaction for a given total enzyme concentration,

$$V_{\max} = k'_3 (E_t) \quad (7-88)$$

the Michaelis-Menten equation takes the familiar form

$$-r_s = \frac{V_{\max} (S)}{K_m + (S)} \quad (7-89)$$

Michaelis-Menten equation

For a given enzyme concentration, a sketch of the rate of disappearance of the substrate is shown as a function of the substrate concentration in Figure 7-11. At low substrate concentration,

$$-r_s \cong \frac{V_{\max} (S)}{K_m}$$

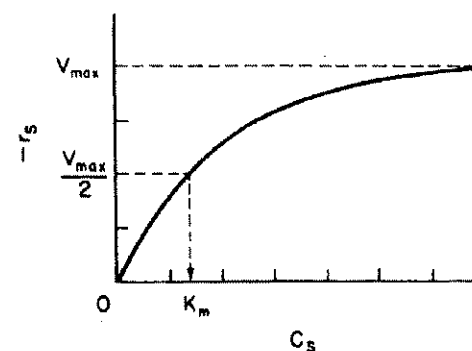


Figure 7-11 Identifying the Michaelis-Menten parameters.

At high substrate concentration,

$$(S) \gg K_m$$

and

$$-r_s \cong V_{\max}$$

Consider the case when the substrate concentration is such that the reaction rate is equal to one-half the maximum rate,

$$-r_s = \frac{V_{\max}}{2}$$

then

$$\frac{V_{\max}}{2} = \frac{V_{\max}(S_{1/2})}{K_m + (S_{1/2})} \quad (7-90)$$

Solving Equation (7-90) for the Michaelis constant yields

$$K_m = (S_{1/2}) \quad (7-91)$$

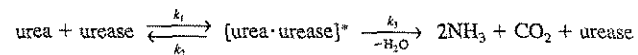
The Michaelis constant is equal to the substrate concentration at which the rate of reaction is equal to one-half the maximum rate.

The parameters V_{\max} and K_m characterize the enzymatic reactions that are described by Michaelis-Menten kinetics. V_{\max} is dependent on total enzyme concentration, whereas K_m is not.

Interpretation of Michaelis constant

Example 7-7 Evaluation of Michaelis-Menten Parameters V_{\max} and K_m

Determine the Michaelis-Menten parameters V_{\max} and K_m for the reaction



The rate of reaction is given as a function of urea concentration in the following table:

C_{urea} (kmol/m ³)	0.2	0.02	0.01	0.005	0.002
$-r_{\text{urea}}$ (kmol/m ³ ·s)	1.08	0.55	0.38	0.2	0.09

Solution

Inverting Equation (7-89) gives us

$$\frac{1}{-r_s} = \frac{(S) + K_m}{V_{\max}(S)} = \frac{1}{V_{\max}} + \frac{K_m}{V_{\max}} \frac{1}{(S)} \quad (\text{E7-7.1})$$

or

$$\frac{1}{-r_{\text{urea}}} = \frac{1}{V_{\max}} + \frac{K_m}{V_{\max}} \left(\frac{1}{C_{\text{urea}}} \right) \quad (\text{E7-7.2})$$

A plot of the reciprocal reaction rate versus the reciprocal urea concentration should be a straight line with an intercept $1/V_{\max}$ and slope K_m/V_{\max} . This type of plot is called a *Lineweaver-Burk plot*. The data in Table E7-7.1 are presented in Figure E7-7.1 in the form of a Lineweaver-Burk plot. The intercept is 0.75, so

$$\frac{1}{V_{\max}} = 0.75 \text{ m}^3 \cdot \text{s} / \text{kmol}$$

Therefore, the maximum rate of reaction is

$$V_{\max} = 1.33 \text{ kmol/m}^3 \cdot \text{s} = 1.33 \text{ mol/dm}^3 \cdot \text{s}$$

TABLE E7-7.1 RAW AND PROCESSED DATA

C_{urea} (kmol/m ³)	$-r_{\text{urea}}$ (kmol/m ³ ·s)	$1/C_{\text{urea}}$ (m ³ /kmol)	$1/-r_{\text{urea}}$ (m ³ ·s/kmol)
0.20	1.08	5.0	0.93
0.02	0.55	50.0	1.82
0.01	0.38	100.0	2.63
0.005	0.20	200.0	5.00
0.002	0.09	500.0	11.11

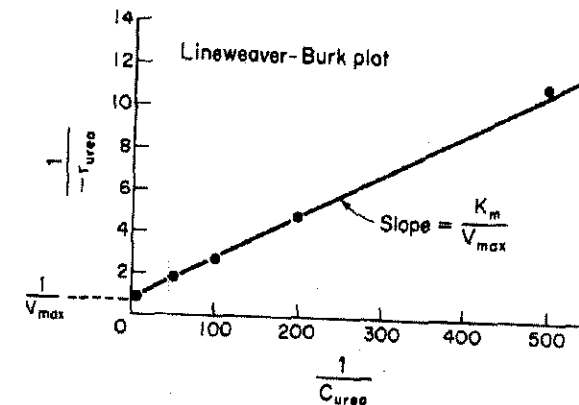


Figure E7-7.1 Lineweaver-Burk Plot.

From the slope, which is 0.02 s, we can calculate the Michaelis constant, K_m :

$$\frac{K_m}{V_{\max}} = \text{slope} = 0.02 \text{ s}$$

$$K_m = 0.0266 \text{ kmol/m}^3$$

Substituting K_m and V_{\max} into Equation (7-89) gives us

$$-r_s = \frac{1.33 C_{\text{urea}}}{0.0266 + C_{\text{urea}}} \quad (\text{E7-7.3})$$

where C_{urea} has units of kmol/m³ and $-r_s$ has units of kmol/m³·s. Levine and LaCourse suggest that the total concentration of urease, (E_t), corresponding to the value of V_{\max} above is approximately 5 g/dm³.

7.4.3 Batch Reactor Calculations

A mole balance on urea in the batch reactor gives

$$-\frac{dN_{\text{urea}}}{dt} = -r_{\text{urea}} V$$

For enzymatic reactions the two key rate-law parameters are V_{\max} and K_m

Mole balance

Because this reaction is liquid phase, the mole balance can be put in the following form:

$$-\frac{dC_{\text{urea}}}{dt} = -r_{\text{urea}} \quad (7-92)$$

The rate law for urea decomposition is

$$\text{Rate law} \quad -r_{\text{urea}} = \frac{V_{\text{max}} C_{\text{urea}}}{K_m + C_{\text{urea}}} \quad (7-93)$$

Substituting Equation (7-93) into Equation (7-92) and then rearranging and integrating, we get

$$\begin{aligned} \text{Combine} \quad t &= \int_{C_{\text{urea}}}^{C_{\text{urea0}}} \frac{dC_{\text{urea}}}{-r_{\text{urea}}} = \int_{C_{\text{urea}}}^{C_{\text{urea0}}} \frac{K_m + C_{\text{urea}}}{V_{\text{max}} C_{\text{urea}}} dC_{\text{urea}} \\ \text{Integrate} \quad t &= \frac{K_m}{V_{\text{max}}} \ln \frac{C_{\text{urea0}}}{C_{\text{urea}}} + \frac{C_{\text{urea0}} - C_{\text{urea}}}{V_{\text{max}}} \end{aligned} \quad (7-94)$$

We can write Equation (7-94) in terms of conversion as

$$C_{\text{urea}} = C_{\text{urea0}}(1 - X)$$

Time to achieve a conversion X in a batch enzymatic reaction

$$t = \frac{K_m}{V_{\text{max}}} \ln \frac{1}{1 - X} + \frac{C_{\text{urea0}} X}{V_{\text{max}}} \quad (7-95)$$

The parameters K_m and V_{max} can readily be determined from batch reactor data by using the integral method of analysis. Dividing both sides of Equation (7-95) by tK_m/V_{max} and rearranging yields

$$\frac{1}{t} \ln \frac{1}{1 - X} = \frac{V_{\text{max}}}{K_m} - \frac{C_{\text{urea0}} X}{K_m t} \quad (7-96)$$

We see that K_m and V_{max} can be determined from the slope and intercept of a plot of $1/t \ln[1/(1 - X)]$ versus X/t . We could also express the Michaelis-Menten equation in terms of the substrate concentration S :

$$\frac{1}{t} \ln \frac{S_0}{S} = \frac{V_{\text{max}}}{K_m} - \frac{S_0 - S}{K_m t} \quad (7-97)$$

where S_0 is the initial concentration of substrate. In cases similar to Equation (7-97) where there is no possibility of confusion, we shall not bother to enclose the substrate or other species in parentheses to represent concentration [i.e., $C_S = (S) = S$]. The corresponding plot in terms of substrate concentration is shown in Figure 7-12.

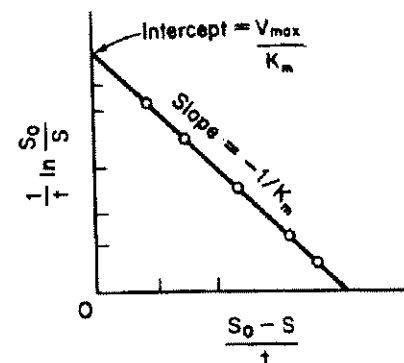


Figure 7-12 Evaluating V_{max} and K_m .

Example 7-8 Batch Enzymatic Reactors

Calculate the time needed to convert 80% of the urea to ammonia and carbon dioxide in a 0.5-dm³ batch reactor. The initial concentration of urea is 0.1 mol/dm³, and the urease concentration is 0.001 g/dm³. The reaction is to be carried out isothermally at the same temperature at which the data in Table E7-7.1 were obtained.

Solution

We can use Equation (7-95),

$$t = \frac{K_m}{V_{\text{max}}} \ln \frac{1}{1 - X} + \frac{C_{\text{urea0}} X}{V_{\text{max}}} \quad (7-95)$$

where $K_m = 0.0266$ g mol/dm³, $X = 0.8$, and $C_{\text{urea0}} = 0.1$ g mol/dm³. V_{max} was 1.33 g mol/dm³·s. However, for the conditions in the batch reactor, the enzyme concentration is only 0.001 g/dm³. Because $V_{\text{max}} = E_t \cdot k_3$, V_{max} for the second enzyme concentration is

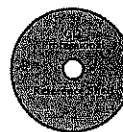
$$V_{\text{max2}} = \frac{E_{t2}}{E_{t1}} V_{\text{max1}} = \frac{0.001}{5} \times 1.33 = 2.66 \times 10^{-4} \text{ mol/s} \cdot \text{dm}^3$$

$$X = 0.8$$

$$\begin{aligned} t &= \frac{0.0266}{0.000266} \ln \frac{1}{0.2} + \frac{(0.8)(0.1)}{0.000266} \\ &= 160.9 + 300.8 \\ &= 461.7 \text{ s} \end{aligned}$$

7.4.4 Inhibition of Enzyme Reactions

Another factor that greatly influences the rates of enzyme-catalyzed reactions in addition to pH is the presence of an inhibitor. The most dramatic consequences of enzyme inhibition are found in living organisms, where the



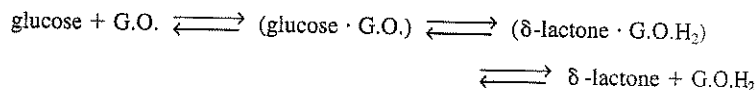
inhibition of any particular enzyme involved in a primary metabolic sequence will render the entire sequence inoperative, resulting in either serious damage or death of the organism. For example, the inhibition of a single enzyme, cytochrome oxidase, by cyanide will cause the aerobic oxidation process to stop; death occurs in a very few minutes. There are also beneficial inhibitors such as the ones used in the treatment of leukemia and other neoplastic diseases.

The three most common types of reversible inhibition occurring in enzymatic reactions are *competitive*, *uncompetitive*, and *noncompetitive*. (See Problem P7-12_B.) The enzyme molecule is analogous to the heterogeneous catalytic surface in that it contains active sites. When competitive inhibition occurs, the substrate and inhibitor are usually similar molecules that compete for the same site on the enzyme. Uncompetitive inhibition occurs when the inhibitor deactivates the enzyme-substrate complex, usually by attaching itself to both the substrate and enzyme molecules of the complex. Noncompetitive inhibition occurs with enzymes containing at least two different types of sites. The inhibitor attaches to only one type of site and the substrate only to the other. Derivation of the rate laws for these three types of inhibition is shown on the CD-ROM.

7.4.5 Multiple Enzyme and Substrate Systems

In the preceding section we discussed how the addition of a second substrate, I, to enzyme-catalyzed reactions could deactivate the enzyme and greatly inhibit the reaction. In the present section we look not only at systems in which the addition of a second substrate is necessary to activate the enzyme, but also other multiple-enzyme and multiple-substrate systems in which cyclic regeneration of the activated enzyme occurs.

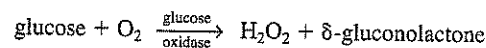
Enzyme Regeneration. The first example considered is the oxidation of glucose (S_r) with the aid of the enzyme glucose oxidase [represented as either G.O. or (E_o)] to give δ -gluconolactone (P):



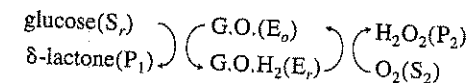
In this reaction, the reduced form of glucose oxidase (G.O.H_2), which will be represented by E_r , cannot catalyze further reactions until it is oxidized back to E_o . This oxidation is usually carried out by adding molecular oxygen to the system so that glucose oxidase, E_o , is regenerated. Hydrogen peroxide is also produced in this oxidation regeneration step:



Overall, the reaction is written

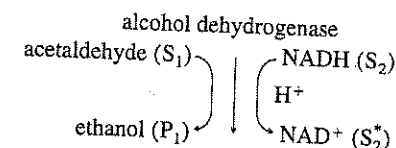


In biochemistry texts, reactions of this type involving regeneration are usually written in the form



Derivation of the rate laws for this reaction sequence is given on the CD-ROM.

Enzyme Cofactors. In many enzymatic reactions, and in particular biological reactions, a second substrate (i.e., species) must be introduced to activate the enzyme. This substrate, which is referred to as a *cofactor* or *coenzyme* even though it is not an enzyme as such, attaches to the enzyme and is most often either reduced or oxidized during the course of the reaction. The enzyme-cofactor complex is referred to as a *holoenzyme*. The inactive form of the enzyme-cofactor complex for a specific reaction and reaction direction is called an *apoenzyme*. An example of the type of system in which a cofactor is used is the formation of ethanol from acetaldehyde in the presence of the enzyme alcohol dehydrogenase (ADH) and the cofactor nicotinamide adenine dinucleotide (NAD):



Derivation of the rate laws for this reaction sequence is given on the CD-ROM.

7.5 Bioreactors

Because enzymatic reactions are involved in the growth of microorganisms, we now proceed to study microbial growth and bioreactors. Not surprisingly, the Monod equation, which describes the growth law for a number of bacteria, is similar to the Michaelis-Menton equation. Consequently, even though bioreactors are not truly homogeneous because of the presence of living cells, we include them in this chapter as a logical progression from enzymatic reactions.

The use of living cells to produce marketable chemical products is becoming increasingly important. By the year 2000, chemicals, agricultural products, and food products produced by biosynthesis will have risen from the 1990 market of \$275 million to around \$17 billion.¹⁵ Both microorganisms and mammalian cells are being used to produce a variety of products, such as insulin, most antibiotics, and polymers. It is expected that in the future a number of organic chemicals currently derived from petroleum will be produced by living cells. The advantages of bioconversions are mild reaction conditions, high yields (e.g., 100% conversion of glucose to gluconic acid with *Aspergillus niger*), that organisms contain several enzymes that can catalyze successive steps in a reaction, and most important, that organisms act as stereospecific

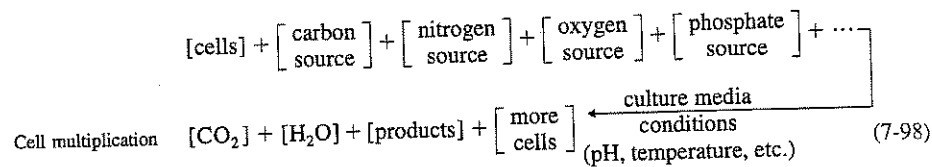
The growth of
biotechnology

¹⁵ *Frontiers in Chemical Engineering*, National Academy Press, Washington, D.C., 1988.

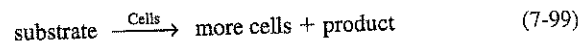
catalysts. A common example of specificity in bioconversion production of a *single* desired isomer that when produced chemically yields a mixture of isomers is the conversion of *cis*-propenylphonic acid to the antibiotic (–) *cis*-1,2-epoxypropyl-phosphonic acid.

In biosynthesis, the cells, also referred to as the *biomass*, consume nutrients to grow and produce more cells and important products. Internally, a cell uses its nutrients to produce energy and more cells. This transformation of nutrients to energy and bioproducts is accomplished through a cell's use of a number of different enzymes (catalysts) in a series of reactions to produce metabolic products. These products can either remain in the cell (intracellular) or be secreted from the cells (extracellular). In the former case the cells must be lysed (ruptured) and the product purified from the whole broth (reaction mixture).

In general, the growth of an aerobic organism follows the equation



A more abbreviated form generally used is



The products in Equation (7-99) include CO₂, water, proteins, and other species specific to the particular reaction. An excellent discussion of the stoichiometry (atom and mole balances) of Equation (7-98) can be found in Wang¹⁶ and in Bailey and Ollis.¹⁷ The substrate culture medium contains all the nutrients (carbon, nitrogen, etc.) along with other chemicals necessary for growth. Because, as we will soon see, the rate of this reaction is proportional to the cell concentration, the reaction is autocatalytic. A rough schematic of a simple batch biochemical reactor and the growth of two types of microorganisms, cocci (i.e., spherical) bacteria and yeast, is shown in Figure 7-13.

7.5.1 Cell Growth

Stages of cell growth in a batch reactor are shown schematically in Figure 7-14. Here, the log of the number of living cells is shown as a function of time. Initially, a small number of cells is inoculated into (i.e., added to) the batch reactor containing the nutrients and the growth process begins.

In phase I, called the lag phase, there is little increase in cell concentration. During the lag phase the cells are adjusting to their new environment,

¹⁶D. C. Wang et al., *Fermentation and Enzyme Technology*, Wiley, New York, 1979.

¹⁷T. J. Bailey and D. Ollis, *Biochemical Engineering*, 2nd ed., McGraw-Hill, New York, 1987.

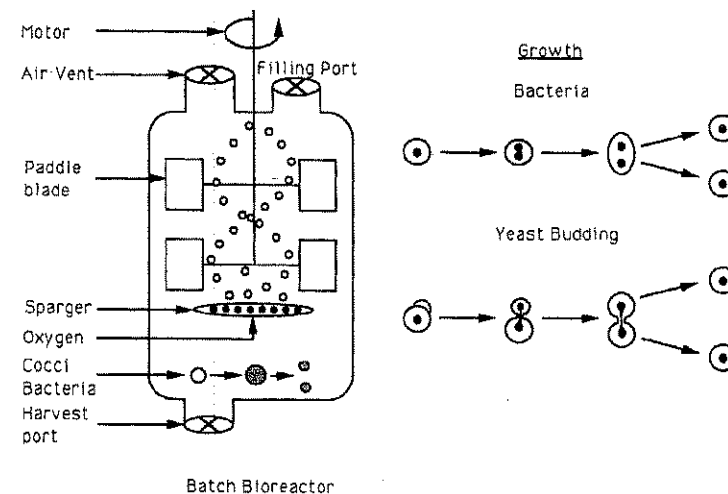


Figure 7-13 Batch bioreactor.

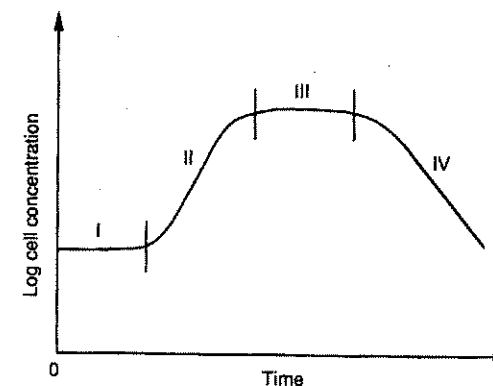


Figure 7-14 Phases of bacteria cell growth.

synthesizing enzymes, and getting ready to begin reproducing. It is during this time that the cells carry out such functions as synthesizing transport proteins for moving the substrate into the cell, synthesizing enzymes for utilizing the new substrate, and beginning the work for replicating the cells' genetic material. The duration of the lag phase depends upon the growth medium (i.e., reactor) from which the inoculum was taken relative to the reaction medium in which it is placed. If the inoculum is similar to the medium of the batch reactor, the lag phase will be almost nonexistent. If, however, the inoculum were placed in a medium with a different nutrient or other contents, or if the inoculum culture were in the stationary or death phase, the cells would have to read-

just their metabolic path to allow them to consume the nutrients in their new environment.

Exponential growth phase

Phase II is called the exponential growth phase owing to the fact that the cell's growth rate is proportional to the cell concentration. In this phase the cells are dividing at the maximum rate because all of the enzyme's pathways for metabolizing the media are in place (as a result of the lag phase) and the cells are able to use the nutrients most efficiently.

Antibiotics produced during the stationary phase

Phase III is the stationary phase, during which the cells reach a minimum biological space where the lack of one or more nutrients limits cell growth. During the stationary phase, the growth rate is zero as a result of the depletion of nutrients and essential metabolites. Many important fermentation products, including most antibiotics, are produced in the stationary phase. For example, penicillin produced commercially using the fungus *Penicillium chrysogenum* is formed only after cell growth has ceased. Cell growth is also slowed by the buildup of organic acids and toxic materials generated during the growth phase.

Death phase

The final phase, Phase IV, is the death phase where a decrease in live cell concentration occurs. This decline is a result of either the toxic by-products and/or the depletion of nutrient supply.

7.5.2 Rate Laws

While many laws exist for the cell growth rate of new cells, that is,

cells + substrate \longrightarrow more cells + product

the most commonly used expression is the *Monod* equation for exponential growth:

Monod equation

$$r_g = \mu C_c \quad (7-100)$$

where r_g = cell growth rate, g/dm³·s

C_c = cell concentration, g/dm³

μ = specific growth rate, s⁻¹

The specific cell growth rate can be expressed as

$$\mu = \mu_{\max} \frac{C_s}{K_s + C_s} \quad \text{s}^{-1} \quad (7-101)$$

where μ_{\max} = a maximum specific growth reaction rate, s⁻¹

K_s = the *Monod* constant, g/dm³

C_s = substrate concentration, g/dm³

For a number of different bacteria, the constant K_s is small, in which case the rate law reduces to

$$r_g = \mu_{\max} C_c \quad (7-102)$$

The growth rate, r_g , often depends on more than one nutrient concentration; however, the nutrient that is limiting is usually the one used in Equation (7-101). Combining Equations (7-100) and (7-101) yields

$$r_g = \mu_{\max} \frac{C_c C_s}{K_s + C_s} \quad (7-103)$$

In many systems the product inhibits the rate of growth. A classic example of this inhibition is in wine-making, where the fermentation of glucose to produce ethanol is inhibited by the product ethanol. There are a number of different equations to account for inhibition; one such rate law takes the form

$$r_g = k_{\text{obs}} \frac{\mu_{\max} C_s C_c}{K_s + C_s} \quad (7-104)$$

where

$$k_{\text{obs}} = \left(1 - \frac{C_p}{C_p^*}\right)^n \quad (7-105)$$

with

C_p^* = product concentration at which all metabolism ceases, g/dm³
 n = empirical constant

For the glucose-to-ethanol fermentation, typical inhibition parameters are

$$n = 0.5 \quad \text{and} \quad C_p^* = 93 \text{ g/dm}^3$$

In addition to the *Monod* equation, two other equations are also commonly used to describe the cell growth rate; they are the *Tessier* equation,

$$r_g = \mu_{\max} \left[1 - \exp\left(-\frac{C_s}{k}\right)\right] C_c \quad (7-106)$$

and the *Moser* equation,

$$r_g = \frac{\mu_{\max} C_c}{(1 + k C_s^{-\lambda})} \quad (7-107)$$

where λ and k are empirical constants determined by a best fit of the data.

The *Moser* and *Tessier* growth laws are often used because they have been found to better fit experimental data at the beginning or end of fermentation. Other growth equations can be found in Dean.¹⁸

The cell death rate is given by

$$r_d = (k_d + k_i C_i) C_c \quad (7-108)$$

where C_i is the concentration of a substance toxic to the cell. The specific death rate constants k_d and k_i refer to the natural death and death due to a toxic

¹⁸A. R. C. Dean, *Growth, Function, and Regulation in Bacterial Cells*, Oxford University Press, London, 1964.

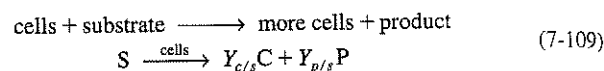
substance, respectively. Representative values of k_d range from 0.1 h^{-1} to less than 0.0005 h^{-1} . The value of k_i depends on the nature of the toxin.

Doubling times

Microbial growth rates are measured in terms of *doubling times*. Doubling time is the time required for a mass of an organism to double. Typical doubling times for bacteria range from 45 minutes to 1 hour but can be as fast as 15 minutes. Doubling times for simple eukaryotes, such as yeast, range from 1.5 to 2 hours but may be as fast as 45 minutes.

7.5.3 Stoichiometry

The stoichiometry for cell growth is very complex and varies with micro-organism/nutrient system and environmental conditions such as pH, temperature, and redox potential. This complexity is especially true when more than one nutrient contributes to cell growth, as is usually the case. We shall focus our discussion on a simplified version for cell growth, one that is limited by only one nutrient in the medium. In general, we have



where the yield coefficients are

$$Y_{c/s} = \frac{\text{mass of new cells formed}}{\text{mass of substrate consumed to produce new cells}}$$

with

$$Y_{c/s} = \frac{1}{Y_{s/c}}$$

The stoichiometric yield coefficient that relates the amount of product formed per mass of substrate consumed is

$$Y_{p/s} = \frac{\text{mass of product formed}}{\text{mass of substrate consumed to form product}}$$

In addition to consuming substrate to produce new cells, part of the substrate must be used just to maintain a cell's daily activities. The corresponding maintenance utilization term is

Cell maintenance

$$m = \frac{\text{mass of substrate consumed for maintenance}}{\text{mass of cells} \cdot \text{time}}$$

A typical value is

$$m = 0.05 \frac{\text{g substrate}}{\text{g dry weight h}} = 0.05 \text{ h}^{-1}$$

The rate of substrate consumption for maintenance whether or not the cells are growing is

$$r_{sm} = mC_c \quad (7-110)$$

The yield coefficient $Y'_{c/s}$ accounts for substrate consumption for maintenance:

$$Y'_{c/s} = \frac{\text{mass of new cells formed}}{\text{mass of substrate consumed}}$$

Product formation can take place during different phases of cell growth. When product is produced only during the growth phase, we can write

$$r_p = Y_{p/c} r_g$$

However, when product is produced during the stationary phase, we can relate product formation to substrate consumption by

$$r_p = Y_{p/s}(-r_s)$$

We now come to the difficult task of relating the rate of nutrient consumption, $-r_s$, to the rates of cell growth, product generation, and cell maintenance. In general, we can write

$$\begin{array}{l} \text{Substrate accounting} \end{array} \quad \left[\begin{array}{c} \text{net rate of} \\ \text{substrate} \\ \text{consumption} \end{array} \right] = \left[\begin{array}{c} \text{rate} \\ \text{consumed} \\ \text{by cells} \end{array} \right] + \left[\begin{array}{c} \text{rate} \\ \text{consumed to} \\ \text{form product} \end{array} \right] + \left[\begin{array}{c} \text{rate} \\ \text{consumed for} \\ \text{maintenance} \end{array} \right]$$

$$-r_s = Y_{s/c} r_g + Y_{s/p} r_p + mC_c \quad (7-111)$$

In a number of cases extra attention must be paid to the substrate balance. If product is produced during the growth phase, it may not be possible to separate out the amount of substrate consumed for growth from that consumed to produce the product. Under these circumstances all the substrate consumed is lumped into the stoichiometric coefficient, $Y_{s/c}$, and the rate of substrate disappearance is

$$-r_s = Y_{s/c} r_g + mC_c \quad (7-112)$$

Product formation
in the growth phase

The corresponding rate of product formation is

The stationary
phase

$$r_p = r_g Y_{p/c} \quad (7-113)$$

Because there is no growth during the stationary phase, it is clear that Equation (7-112) cannot be used to account for substrate consumption, nor can the rate of product formation be related to the growth rate [e.g., Equation (7-113)]. Many antibiotics, such as penicillin, are produced in the stationary phase. In this phase, the nutrient consumed for growth has become virtually exhausted and a different nutrient, called the secondary nutrients, is used for cell maintenance and to produce the desired product. Usually, the rate law for product formation during the stationary phase is similar in form to the Monod equation, that is,

Product formation
in the stationary
phase

$$r_p = \frac{k_p C_{sn} C_c}{K_{sn} + C_{sn}} \quad (7-114)$$

where C_{sn} = concentration of the secondary nutrient, g/dm³
 k_p = specific rate constant with product, s⁻¹
 C_c = cell concentration, g/dm³
 K_{sn} = constant, g/dm³
 $r_p = Y_{p/sn}(-r_{sn})$

The net rate of substrate consumption during the stationary phase is

$$\begin{aligned} -r_{sn} &= mC_c + Y_{sn/p} r_p \\ &= mC_c + \frac{Y_{sn/p} k_p C_{sn} C_c}{K_{sn} + C_{sn}} \end{aligned} \quad (7-115)$$

Because the desired product can be produced when there is no cell growth, it is always best to relate the product concentration to the change in substrate concentration. For a batch system the concentration of product, C_p , formed after a time t can be related to the substrate concentration, C_s , at that time.

$$C_p = Y_{p/s}(C_{s0} - C_s) \quad (7-116)$$

We have considered two limiting situations for relating substrate consumption to cell growth and product formation; product formation only during the growth phase and product formation only during the stationary phase. An example where neither of these situations apply is fermentation using lactobacillus, where lactic acid is produced during both the logarithmic growth and stationary phase.

7.5.4 Mass Balances

There are two ways that we could account for the growth of microorganisms. One is to account for the number of living cells and the other is to account for the mass of the living cells. We shall use the latter. A mass balance on the microorganism in a CSTR (chemostat) (shown in Figure 7-15) of constant volume is

$$\begin{aligned} \left[\begin{array}{c} \text{rate of} \\ \text{accumulation} \\ \text{of cells,} \\ \text{g/s} \end{array} \right] &= \left[\begin{array}{c} \text{rate of} \\ \text{cells} \\ \text{entering,} \\ \text{g/s} \end{array} \right] - \left[\begin{array}{c} \text{rate of} \\ \text{cells} \\ \text{leaving,} \\ \text{g/s} \end{array} \right] + \left[\begin{array}{c} \text{net rate of} \\ \text{generation} \\ \text{of live cells,} \\ \text{g/s} \end{array} \right] \quad (7-117) \\ V \frac{dC_c}{dt} &= v_0 C_{c0} - v C_c + (r_g - r_d)V \end{aligned}$$

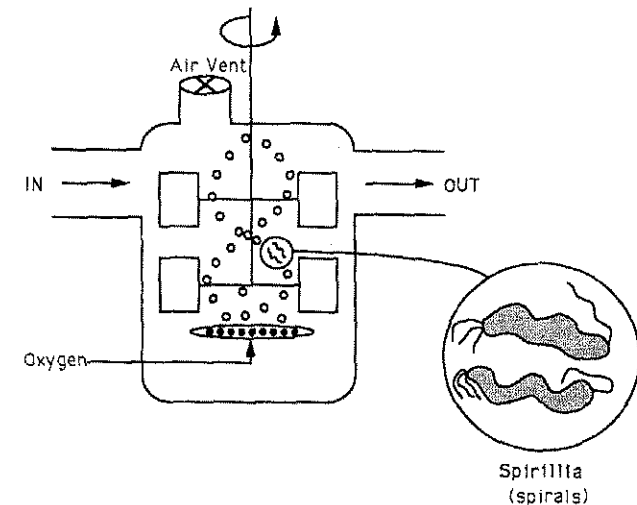


Figure 7-15 Bioreactor.

The corresponding substrate balance is

$$\begin{aligned} \left[\begin{array}{c} \text{rate of} \\ \text{accumulation} \\ \text{of substrate,} \\ \text{g/s} \end{array} \right] &= \left[\begin{array}{c} \text{rate of} \\ \text{substrate} \\ \text{entering,} \\ \text{g/s} \end{array} \right] - \left[\begin{array}{c} \text{rate of} \\ \text{substrate} \\ \text{leaving,} \\ \text{g/s} \end{array} \right] + \left[\begin{array}{c} \text{rate of} \\ \text{substrate} \\ \text{generation,} \\ \text{g/s} \end{array} \right] \quad (7-118) \\ V \frac{dC_s}{dt} &= v_0 C_{s0} - v C_s + r_s V \end{aligned}$$

In most systems the entering microorganism concentration C_{c0} is zero. For a batch system the mass balances develop as follows:

Cell

Batch

$$V \frac{dC_c}{dt} = r_g V - r_d V$$

Dividing by the reactor volume V gives

$$\frac{dC_c}{dt} = r_g - r_d \quad (7-119)$$

Substrate

The rate of disappearance of substrate, $-r_s$, results from substrate used for cell growth and substrate used for cell maintenance,

The mass balances

$$V \frac{dC_s}{dt} = r_s V = Y_{s/c}(-r_g)V - mC_c V \quad (7-120)$$

Dividing by V yields

Growth phase

$$\frac{dC_s}{dt} = Y_{s/c}(-r_g) - mC_c$$

For cells in the stationary phase, where there is no growth, cell maintenance and product formation are the only reactions to consume the substrate. Under these conditions the substrate balance, Equation (7-118), reduces to

Stationary phase

$$V \frac{dC_s}{dt} = -mC_c V + Y_{s/p}(-r_p)V \quad (7-121)$$

Typically, r_p will have the same form of the rate law as r_g [e.g., Equation (7-114)].

Batch stationary growth phase

Product

The rate of product formation, r_p , can be related to the rate of substrate consumption through the following balance:

$$V \frac{dC_p}{dt} = r_p V = Y_{p/s}(-r_s)V \quad (7-122)$$

During the growth phase we could also relate the rate of formation of product, r_p , to the cell growth rate, r_g . The coupled first-order ordinary differential equations above can be solved by a variety of numerical techniques.

Example 7-9 Bacteria Growth in a Batch Reactor

Glucose-to-ethanol fermentation is to be carried out in a batch reactor using an organism such as *Saccharomyces cerevisiae*. Plot the concentrations of cells, substrate, and product and growth rates as functions of time. The initial cell concentration is 1.0 g/dm³ and the substrate (glucose) concentration is 250 g/dm³.

Additional data [partial source: R. Miller and M. Melick, *Chem. Eng.*, Feb. 16, p. 113 (1987)]:

$$\begin{aligned} C_p^* &= 93 \text{ g/dm}^3 & Y_{c/s} &= 0.08 \text{ g/g} \\ n &= 0.52 & Y_{p/s} &= 0.45 \text{ g/g (est.)} \\ \mu_{\max} &= 0.33 \text{ h}^{-1} & Y_{p/c} &= 5.6 \text{ g/g (est.)} \\ K_s &= 1.7 \text{ g/dm}^3 & k_d &= 0.01 \text{ h}^{-1} \\ m &= 0.03 \text{ (g substrate)/(g cells} \cdot \text{h)} \end{aligned}$$

Solution**1. Mass balances:**

$$\text{Cells:} \quad V \frac{dC_c}{dt} = (r_g - r_d)V \quad (E7-9.1)$$

$$\text{Substrate:} \quad V \frac{dC_s}{dt} = Y_{s/c}(-r_g)V - r_{sm}V \quad (E7-9.2)$$

$$\text{Product:} \quad V \frac{dC_p}{dt} = Y_{p/c}(r_g)V \quad (E7-9.3)$$

2. Rate laws:

$$r_g = \mu_{\max} \left(1 - \frac{C_p}{C_p^*}\right)^{0.52} \frac{C_c C_s}{K_s + C_s} \quad (E7-9.4)$$

$$r_d = k_d C_c \quad (E7-9.5)$$

$$r_{sm} = mC_c \quad (7-110)$$

3. Stoichiometry:

$$r_p = Y_{p/c} r_g \quad (E7-9.6)$$

4. Combining gives

$$\frac{dC_c}{dt} = \mu_{\max} \left(1 - \frac{C_p}{C_p^*}\right)^{0.52} \frac{C_c C_s}{K_s + C_s} - k_d C_c \quad (E7-9.7)$$

$$\frac{dC_s}{dt} = -Y_{s/c} \mu_{\max} \left(1 - \frac{C_p}{C_p^*}\right)^{0.52} \frac{C_c C_s}{K_s + C_s} - mC_c \quad (E7-9.8)$$

$$\frac{dC_p}{dt} = Y_{p/c} r_g$$

These equations were solved on an ODE equation solver (see Table E7-9.1). The results are shown in Figure E7-9.1 for the parameter values given in the problem statement.

TABLE E7-9.1. POLYMATH PROGRAM

Equations:	Initial Values:
d(cc)/d(t)=rg-rd	1
d(cs)/d(t)=ysc*(-rg)-rsm	250
d(cp)/d(t)=rg*ypc	0
rd=cc*.01	
ysc=1/.08	
ypc=5.6	
ks=1.7	
m=.03	
umax=.33	
rsm=m*cc	
kobs=(umax*(1-cp/93)^.52)	
rg=kobs*cc*cs/(ks+cs)	
t0 = 0, tF = 12	

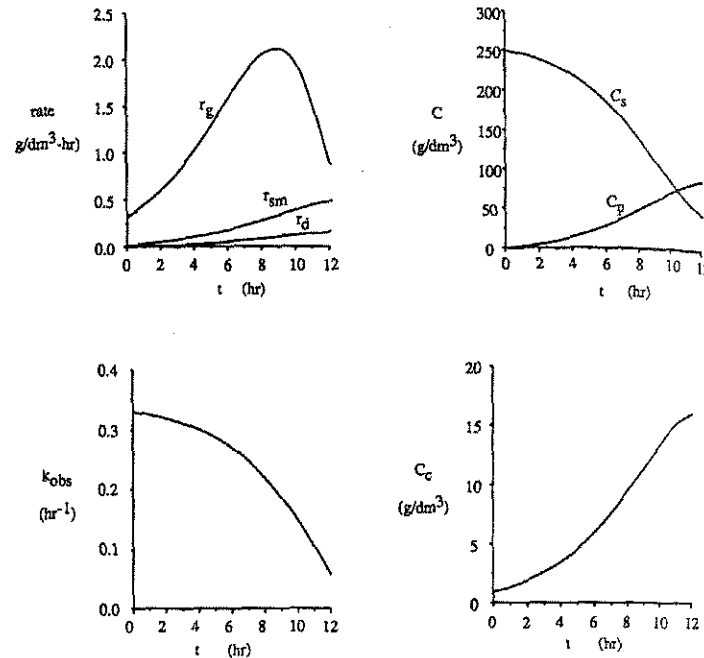


Figure E7-9.1 Concentrations and rates as a function of time.

7.5.5 Chemostats

Chemostats are essentially CSTRs that contain microorganisms. A typical chemostat is shown in Figure 7-16, along with the associated monitoring equipment and pH controller. One of the most important features of the chemostat is that it allows the operator to control the cell growth rate. This control of the growth rate is achieved by adjusting the volumetric feed rate (dilution rate).

7.5.6 Design Equations

In this section we return to mass equations on the cells [Equation (7-117)] and substrate [Equation (7-118)] and consider the case where the volumetric flow rates in and out are the same and that no live (i.e., viable) cells enter the chemostat. We next define a parameter common to bioreactors called the dilution rate, D . The dilution rate is

$$D = \frac{v_0}{V}$$

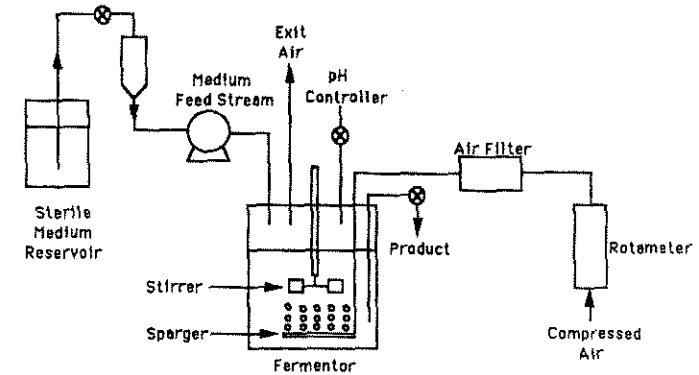


Figure 7-16 Chemostat system.

and is simply the reciprocal of the space time τ . Dividing Equations (7-117) and (7-118) by V and using the definition of the dilution rate, we have

$$\text{accumulation} = \text{in} - \text{out} + \text{generation}$$

CSTR mass
balances

$$\text{Cell: } \frac{dC_c}{dt} = 0 - DC_c + (r_g - r_d) \quad (7-123)$$

$$\text{Substrate: } \frac{dC_s}{dt} = DC_{s0} - DC_s + r_s \quad (7-124)$$

Using the Monod equation, the growth rate is determined to be

$$r_g = \mu C_c \quad (7-100)$$

where

$$\mu = \frac{\mu_{\max} C_s}{K_s + C_s} \quad (7-101)$$

For steady-state operation we have

$$DC_c = r_g - r_d \quad (7-125)$$

and

$$D(C_{s0} - C_s) = r_s \quad (7-126)$$

We now neglect the death rate, r_d , and combine Equations (7-100) and (7-125) for steady-state operation to obtain the mass flow rate of cells out of the system, \dot{m}_c .

$$\dot{m}_c = C_c v_0 = r_g V = \mu C_c V \quad (7-127)$$

After we divide by $C_c V$,

Dilution rate

$$D = \mu \quad (7-128)$$

An inspection of Equation (7-128) reveals that the specific growth rate of the cells *can be controlled* by the operator by controlling the dilution rate D . Using Equation (7-101) to substitute for μ in terms of the substrate concentration and then solving for the steady-state substrate concentration yields

$$C_s = \frac{DK_s}{\mu_{\max} - D} \quad (7-129)$$

Assuming that a single nutrient is limiting, cell growth is the only process contributing to substrate utilization, and that cell maintenance can be neglected, the stoichiometry is

$$-r_s = r_g Y_{s/c} \quad (7-130)$$

$$C_c = Y_{c/s}(C_{s0} - C_s) \quad (7-131)$$

Substituting for C_s using Equation (7-129), we obtain

$$C_c = \frac{Y_{c/s}(C_{s0} + K_s)}{\mu_{\max} - D} \left(\frac{\mu_{\max} C_{s0}}{K_s + C_{s0}} - D \right) \quad (7-132)$$

7.5.7 Wash-out

To learn the effect of increasing the dilution rate, we combine Equations (7-123) and (7-100) and set $r_d = 0$ to get

$$\frac{dC_c}{dt} = (\mu - D)C_c \quad (7-133)$$

We see that if $D > \mu$, then dC_c/dt will be negative and the cell concentration will continue to decrease until we reach a point where all cells will be washed out:

$$C_c = 0$$

The dilution rate at which wash-out will occur is obtained from Equation (7-132) by setting $C_c = 0$.

Flow rate at which
wash-out occurs

$$D_{\max} = \frac{\mu_{\max} C_{s0}}{K_s + C_{s0}} \quad (7-134)$$

We next want to determine the other extreme for the dilution rate, which is the rate of maximum cell production. The cell production rate per unit volume of reactor is the mass flow rate of cells out of the reactor (i.e., $\dot{m}_c = C_c v_0$) divided by the volume V , or

$$\frac{v_0 C_c}{V} = DC_c$$

Substituting for C_c yields

$$DC_c = DY_{c/s} \left(C_{s0} - \frac{DK_s}{\mu_{\max} - D} \right) \quad (7-135)$$

Figure 7-17 shows production rate, cell concentration, and substrate concentration as functions of dilution rate. We observe a maximum in the production rate and this maximum can be found by differentiating production with respect to the dilution rate D :

$$\frac{d(DC_c)}{dD} = 0$$

Maximum rate of
cell production
(DC_c)

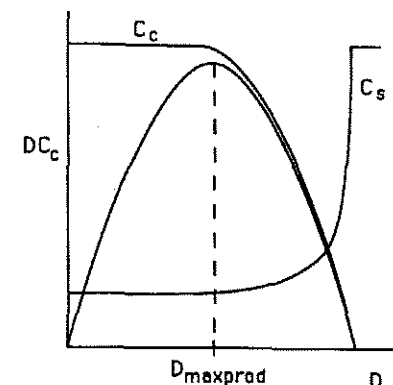


Figure 7-17 Cell concentration and production rate as a function of dilution rate.

Then

Maximum rate of
cell production

$$D_{\max\text{prod}} = \mu_{\max} \left(1 - \sqrt{\frac{K_s}{K_s + C_{s0}}} \right) \quad (7-136)$$



7.5.8 Oxygen-Limited Fermentation

Oxygen is necessary for all aerobic fermentations (by definition). Maintaining the appropriate concentration of dissolved oxygen in fermentation is important for efficient operation of a fermentor. For oxygen-limited systems, it is necessary to design a fermentor to maximize the oxygen transfer between the injected air bubble and the cell. Typically, a fermentor contains a gas sparger, heat transfer surfaces, and an impeller, for a batch reactor. A chemostat has a similar configuration with the addition of inlet and outlet streams. The CD-ROM discusses the transport steps from the bulk liquid to and within the microorganism. A series of mass transfer correlations are also given.

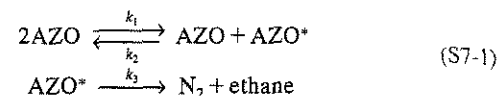
7.5.9 Scale-up

Scale-up for the growth of microorganisms is usually based on maintaining a constant dissolved oxygen concentration in the liquid (broth), indepen-

dent of reactor size. Guidelines for scaling from a pilot-plant bioreactor to a commercial plant reactor are given on the CD-ROM. One key to a scale-up is to have the speed of the end (tip) of the impeller equal to the velocity in both the laboratory pilot reactor and the full-scale plant reactor. If the impeller speed is too rapid, it can lyse the bacteria; if the speed is too slow, the reactor contents will not be well mixed. Typical tip speeds range from 5 to 7 m/s.

SUMMARY

1. The azomethane (AZO) decomposition mechanism is



The rate expression for the mechanism of this decomposition,

$$r_{\text{N}_2} = \frac{k(\text{AZO})^2}{1 + k'(\text{AZO})} \quad (\text{S7-2})$$

exhibits first-order dependence with respect to AZO at high AZO concentrations and second-order dependence with respect to AZO at low AZO concentrations.

2. In the PSSH, we set the rate of formation of the active intermediates equal to zero. If the active intermediate A^* is involved in m different reactions, we set it to

$$r_{A^*, \text{net}} \equiv \sum_{i=1}^m r_{A^*, i} = 0 \quad (\text{S7-3})$$

This approximation is justified when the active intermediate is highly reactive and present in low concentrations.

3. Polymerization: (step reactions and chain reactions)

- (a) Steps: initiation, propagation, transfer, termination.
(b) The fraction of functional groups that have reacted is

$$p = \frac{M_o - M}{M_o}$$

- (c) The degree of polymerization is

$$\bar{X}_n = \frac{1}{1-p} \quad (\text{S7-4})$$

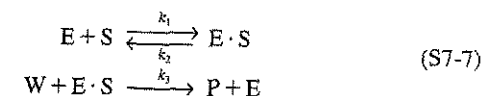
- (d) The Flory distribution for the mole fraction is

$$y_j = (1-p)p^{j-1} \quad (\text{S7-5})$$

and for the weight fraction is

$$w_j = j(1-p)^2 p^{j-1} \quad (\text{S7-6})$$

4. The enzymatic reaction for the decomposition of urea, S, catalyzed by urease, E, is



It follows Michaelis-Menten kinetics and the rate expression is

$$-r_s = \frac{V_{\max} S}{S + K_m} \quad (\text{S7-8})$$

where V_{\max} is the maximum rate of reaction for a given enzyme concentration and K_m is the Michaelis constant.

5. The total amount of a given enzyme in the system is the sum of the free enzyme, E, and the bound enzyme, $\text{E} \cdot \text{S}$:

$$E_t = \text{E} \cdot \text{S} + \text{E} \quad (\text{S7-9})$$

To arrive at Equation (S7-8) we treat each reaction as elementary, apply the PSSH to the complex, and use Equation (S7-9).

6. Bioreactors:

cells + substrate \longrightarrow more cells + product

- (a) Phases of bacteria growth:

I. Lag II. Exponential III. Stationary IV. Death

- (b) Monod growth rate law:

$$r_g = \mu_{\max} \frac{C_c C_s}{K_s + C_s} \quad (\text{S7-10})$$

- (c) Stoichiometry:

$$Y_{c/s} = \frac{\text{mass of new cells formed}}{\text{substrate consumed to produce new cells}}$$

- (d) Unsteady-state mass balance on a chemostat:

$$\frac{dC_c}{dt} = \frac{C_{c0} - C_c}{\tau} + r_g - r_d \quad (\text{S7-11})$$

$$\frac{dC_s}{dt} = \frac{C_{s0} - C_s}{\tau} + r_s \quad (\text{S7-12})$$

$$-r_s = Y_{s/c} r_g + Y_{s/p} r_p + m C_c \quad (\text{S7-13})$$

QUESTIONS AND PROBLEMS

The subscript to each of the problem numbers indicates the level of difficulty: A, least difficult; D, most difficult.

A = ● B = ■ C = ◆ D = ◆◆

In each of the questions and problems below, rather than just drawing a box around your answer, write a sentence or two describing how you solved the problem, the assumptions you made, the reasonableness of your answer, what you learned, and any other facts that you want to include. You may wish to refer to W. Strunk and E. B. White, *The Elements of Style* (New York: Macmillan, 1979) and Joseph M. Williams, *Style: Ten Lessons in Clarity & Grace* (Glenview, Ill.: Scott, Foresman, 1989) to enhance the quality of your sentences. See the Preface for additional generic parts (x), (y), (z) to the home problems.

P7-1C Read over all of this chapter's problems. Make up an original problem that uses the concepts presented in this chapter. To obtain a solution:

- Make up your data and reaction.
- Use a real reaction and real data.

See R. M. Felder, *Chem. Eng. Educ.*, 19(4), 176 (1985).

P7-2A What if...

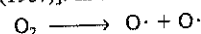
- you carried out the ethane reaction in Example 7-2 at 1500 K or 2000 K? Would the PSSH still be valid? Can you find a temperature at which the PSSH is not a good approximation? Explain.

[Hint: Calculate different ratios of radicals (e.g., $\text{CH}_3\cdot/\text{H}\cdot$, $\text{CH}_3\cdot/\text{C}_2\text{H}_5\cdot$, etc.).]

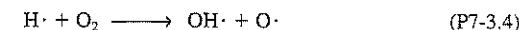
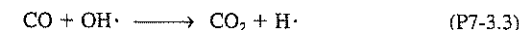
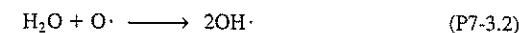
- you could choose from a number of different initiators ($\text{I}_2 \xrightarrow{k_0} 2\text{I}\cdot$): fast to slow, $k_0 = 0.01 \text{ s}^{-1}$, $k_0 = 0.0001 \text{ s}^{-1}$, and $k_0 = 0.00001 \text{ s}^{-1}$, and initiator concentrations, 10^{-1} to 10^{-5} M ? What would guide your selection? (Hint: Plot M vs. t .)
- the enzymatic reaction in Example 7-7 were exothermic? What would be the effect of raising or lowering the temperature of the rate law parameters on the overall rate?
- the enzymatic reaction in Example 7-8 were carried out in a CSTR with a space time of 400 s? What conversion would be achieved? How would your answer change for two CSTRs in series, with $\tau = 200 \text{ s}$ for each? What if both the total enzyme concentration and the substrate concentration were increased by a factor of 4 in the CSTR with $\tau = 400 \text{ s}$?
- you were asked to carry out the bioreaction in Example 7-9 at higher and lower temperatures? What do you think the substrate, cell, and product concentrations would look like? Sketch each as a function of time for different temperatures. Discuss the reasonableness of assumptions you made to arrive at your curves. What is the relationship between C_p^* and $Y_{p/S}$ for which the final cell concentration is invariant? Can an equation for the washout dilution rate be derived for the Tessier Eqn.? If so what is it?

P7-3B

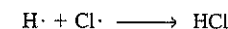
(Flame retardants) Hydrogen radicals are important to sustaining combustion reactions. Consequently, if chemical compounds are introduced that can scavenge the hydrogen radicals, the flames can be extinguished. While many reactions occur during the combustion process, we shall choose CO flames as a model system to illustrate the process [S. Senkan et al., *Combustion and Flame*, 69, p. 113 (1987)]. In the absence of inhibitors



(P7-3.1)



The last two reactions are rapid compared to the first two. When HCl is introduced to the flame, the following additional reactions occur:



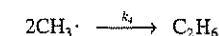
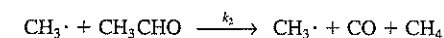
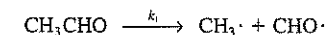
Assume that all reactions are elementary and that the PSSH holds for the $\text{O}\cdot$, $\text{OH}\cdot$, and $\text{Cl}\cdot$ radicals.

- Derive a rate law for the consumption of CO when no retardant is present.
- Derive an equation for the concentration of $\text{H}\cdot$ as a function of time assuming constant concentration of O_2 , CO, and H_2O for both uninhibited combustion and combustion with HCl present. Sketch $\text{H}\cdot$ versus time for both cases.

(c) Sketch a reaction pathway diagram for this reaction.

More elaborate forms of this problem can be found in Chapter 6, where the PSSH is not invoked.

P7-4A The pyrolysis of acetaldehyde is believed to take place according to the following sequence:

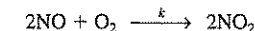


- Derive the rate expression for the rate of disappearance of acetaldehyde, $-r_{\text{Ac}}$.

(b) Under what conditions does it reduce to Equation (7-2)?

(c) Sketch a reaction pathway diagram for this reaction.

P7-5B The gas-phase homogeneous oxidation of nitrogen monoxide (NO) to dioxide (NO_2),



is known to have a form of third-order kinetics which suggests that the reaction is elementary as written, at least for low partial pressures of the nitrogen oxides. However, the rate constant k actually decreases with increasing absolute temperature, indicating an apparently negative activation energy. Because the activation energy of any elementary reaction must be positive, some explanation is in order.

Provide an explanation, starting from the fact that an active intermediate species, NO_3 , is a participant in some other known reactions that involve oxides of nitrogen.

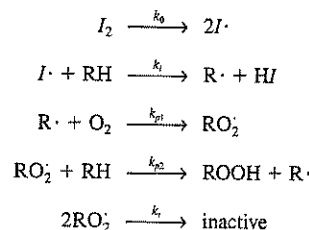
P7-6B For the decomposition of ozone in an inert gas M, the rate expression is

$$-r_{\text{O}_3} = \frac{k(\text{O}_3)^2(\text{M})}{(\text{O}_2)(\text{M}) + k'(\text{O}_3)}$$

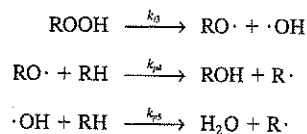
Suggest a mechanism.



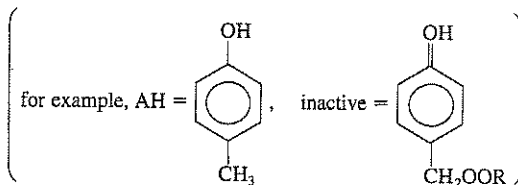
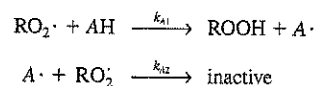
- P7-7c** (Tribiology) One of the major reasons for engine oil degradation is the oxidation of the motor oil. To retard the degradation process, most oils contain an antioxidant [see *Ind. Eng. Chem.* 26, 902 (1987)]. Without an inhibitor to oxidation present, the suggested mechanism at low temperatures is



where I_2 is an initiator and RH is the hydrocarbon in the oil. When the temperature is raised to 100°C , the following additional reaction occurs as a result of the decomposition of the unstable $ROOH$:



When an antioxidant is added to retard degradation at low temperatures, the following additional termination steps occur:

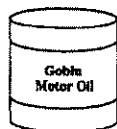


Derive a rate law for the degradation of the motor oil in the absence of an antioxidant at

- (a) Low temperatures.
(b) High temperatures.

Derive a rate law for the rate of degradation of the motor oil in the presence of an antioxidant for

- (c) Low temperatures.
(d) High temperatures. Here assume that the inactive products formed with antioxidant do not decompose (probably a bad assumption).
(e) How would your answer to part (a) change if the radicals $I\cdot$ were produced at a constant rate in the engine and then found their way into the oil?
(f) Sketch a reaction pathway diagram for both high and low temperatures, with and without antioxidant.



Effective Lubricant Design

- P7-8A** Consider the application of the PSSH to epidemiology. We shall treat each of the following steps as elementary in that the rate will be proportional to the number of people in a particular state of health. A healthy person, H , can become ill, I , spontaneously,



or he may become ill through contact with another ill person:



The ill person may become healthy:



or he may expire:



The reaction given in Equation (P7-8.4) is normally considered completely irreversible, although the reverse reaction has been reported to occur.

- (a) Derive an equation for the death rate.
(b) At what concentration of healthy people does the death rate become critical? [Ans.: When $[H] = (k_3 + k_4)/k_2$.]
(c) Comment on the validity of the PSSH under the conditions of part (b).
(d) If $k_1 = 10^{-5} \text{ h}^{-1}$, $k_2 = 10^{-7} (\text{people} \cdot \text{h})^{-1}$, $k_3 = 5 \times 10^{-6} \text{ h}$, $k_4 = 10^{-7} \text{ h}$, and $H_0 = 10^9$ people, plot H , I , and D versus time. Vary k_i and describe what you find. Check with your local *disease control center* or search the WWW to modify the model and/or substitute appropriate values of k_i .

- P7-9c** (Postacidification in yogurt) Yogurt is produced by adding two strains of bacteria (*Lactobacillus bulgaricus* and *Streptococcus thermophilus*) to pasteurized milk. At temperatures of 110°F , the bacteria grow and produce lactic acid. The acid contributes flavor and causes the proteins to coagulate, giving the characteristic properties of yogurt. When sufficient acid has been produced (about 0.90%), the yogurt is cooled and stored until eaten by consumers. A lactic acid level of 1.10% is the limit of acceptability. One limit on the shelf life of yogurt is "postacidification," or continued production of acid by the yogurt cultures during storage. The table that follows shows acid production (% lactic acid) in yogurt versus time at four different temperatures.

Time (days)	35°F	40°F	45°F	50°F
1	1.02	1.02	1.02	1.02
14	1.03	1.05	1.14	1.19
28	1.05	1.06	1.15	1.24
35	1.09	1.10	1.22	1.26
42	1.09	1.12	1.22	1.31
49	1.10	1.12	1.22	1.32
56	1.09	1.13	1.24	1.32
63	1.10	1.14	1.25	1.32
70	1.10	1.16	1.26	1.34

Acid production by yogurt cultures is a complex biochemical process. For the purpose of this problem, assume that acid production follows first-order kinetics with respect to the consumption of lactose in the yogurt to produce lactic acid. At the start of acid production the lactose concentration is



Chemical Engineering
in the Food Industry

about 1.5%, the bacteria concentration is 10^{11} cells/dm³, and the acid concentration at which all metabolic activity ceases is 1.4% lactic acid.

- Determine the activation energy for the reaction.
- How long would it take to reach 1.10% acid at 38°F?
- If you left yogurt out at room temperature, 77°F, how long would it take to reach 1.10% lactic acid?
- Assuming that the lactic acid is produced in the stationary state, do the data fit any of the modules developed in this chapter?

[Problem developed by General Mills, Minneapolis, Minnesota]

P7-10c

The enzymatic hydrolyzation of fish oil extracted from crude eel oil has been carried out using lipase L (*Proc. 2nd Joint China/USA Chemical Engineering Conference*, Vol. III, p. 1082, 1997). One of the desired products is docosahexaenoic acid, which is used as a medicine in China. For 40 mg of enzyme the Michaelis constant is 6.2×10^{-2} (mL/mL) and V_{\max} is $5.6 \mu\text{mol/mL} \cdot \text{min}$. Calculate the time necessary to reduce the concentration of fish oil from 1.4% to 0.2 vol %. Note: There may be an inconsistency in the article. The half life for an initial volume of 25% fish oil is stated to be 4.5 days. However, this yields a different initial fish oil concentration one finds from looking in the literature. Search the web for *fish oil*. Suggest a way to resolve this controversy.

P7-11b

Beef catalase has been used to accelerate the decomposition of hydrogen peroxide to yield water and oxygen [*Chem. Eng. Educ.*, 5, 141 (1971)]. The concentration of hydrogen peroxide is given as a function of time for a reaction mixture with a pH of 6.76 maintained at 30°C.

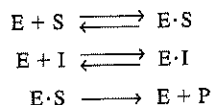
t (min)	0	10	20	50	100
$C_{\text{H}_2\text{O}_2}$ (mol/L)	0.02	0.01775	0.0158	0.0106	0.005

- Determine the Michaelis-Menten parameters V_{\max} and K_m .
- If the total enzyme concentration is tripled, what will the substrate concentration be after 20 min?
- How could you make this problem more difficult?

P7-12b

In this problem three different types of reaction inhibition are explored:

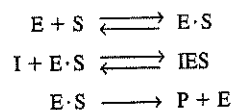
- In competitive inhibition, an inhibitor adsorbs on the same type of site as the substrate. The resulting inhibitor-enzyme complex is inactive. Show that the rate law for competitive inhibition



is

$$r_p = \frac{V_{\max} S}{S + K_m (1 + I/K_i)}$$

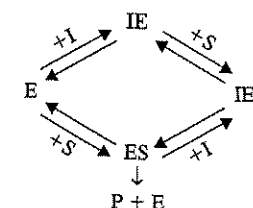
- In uncompetitive inhibition the inhibitor attaches itself to enzyme-substrate complex, rendering it inactive. Show that for uncompetitive inhibition,



the rate law is

$$r_p = \frac{V_{\max} S}{K_m + S (1 + I/K_i)}$$

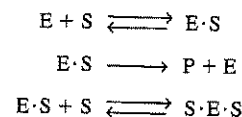
- In noncompetitive inhibition, the inhibitor adsorbs itself to a different type of site than the substrate to render the enzyme-substrate complex inactive. Assuming that all concentrations of a species can be expressed by their equilibrium concentrations, show that for noncompetitive inhibition



the rate law is

$$r_p = \frac{V_{\max} S}{(S + K_m)(1 + I/K_i)}$$

- Sketch three different inhibitions on a Lineweaver-Burk plot.
- P7-13b It has been observed that substrate inhibition occurs in the following enzymatic reaction:



- Show that the rate law for the sequence above is consistent with the plot in Figure P7-13 of $-r_s$ (mmol/L · min) versus the substrate concentration S (mmol/L). (Refer to Problem P7-12.)

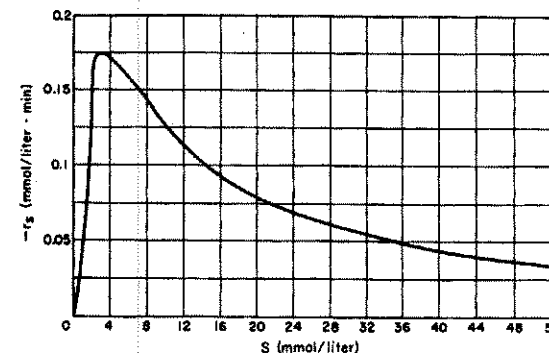


Figure P7-13

- (b) If this reaction is carried out in a CSTR that has a volume of 1000 L, to which the volumetric flow rate is 3.2 L/min, determine the three possible steady states, noting, if possible, which are stable. The entrance concentration of the substrate is 50 mmol/L.
- (c) What is the highest conversion possible for this CSTR when operated at the conditions specified above?

P7-14_B The following data on bakers' yeast in a particular medium at 23.4°C and various oxygen partial pressures were obtained:

P_{O_2}	Q_{O_2} (no sulfanilamide)	Q_{O_2} (20 mg sulfanilamide/mL added to medium)
0.0	0.0	0.0
0.5	23.5	17.4
1.0	33.0	25.6
1.5	37.5	30.8
2.5	42.0	36.4
3.5	43.0	39.6
5.0	43.0	40.0

P_{O_2} = oxygen partial pressure, mmHg; Q_{O_2} = oxygen uptake rate, μL of O_2 per hour per mg of cells.

- (a) Calculate the Q_{O_2} maximum (V_{\max}), and the Michaelis-Menten constant K_m . (Ans.: $V_{\max} = 52.63 \mu\text{L } O_2/\text{h} \cdot \text{mg cells}$.)
- (b) By use of the Lineweaver-Burk plot, determine whether sulfanilamide is a competitive or noncompetitive inhibitor to O_2 uptake. (Refer to Problem P7-12).

(University of Pennsylvania)

- P7-15** (a) Use the supplementary reading to give three examples each of polymers formed by step polymerization and by chain polymerization. Describe the monomers, structural unit(s) and repeating unit in each case.
- (b) Plot y_j , w_j as a function of j for degrees of polymerization of 5, 10, and 20. Plot \bar{P}_{10} as a function of conversion of function groups, P .
- (c) Plot y_j and w_j as a function of j for free radical termination by combination for $P = 0.8$, $p = 0.9$ and $p = 0.95$.
- (d) Determine the molecular weight distribution for the formation of polystyrene for an initiator concentration of 10^{-3} molar and a monomer concentration of 3 molar. What are \bar{M}_n , \bar{M}_w , and the polydispersity, D , after 40 hrs? How would the \bar{M}_n change if chain transfer were neglected?
- (e) The polymerization of styrene is carried out in a batch reactor. Plot the mole fraction of polystyrene of chain length 10 as a function of time for an initial concentration of 3M and 0.01M of monomer an initiator respectively. The solvent concentration is 10 molar.

P7-16_B The instantaneous number-average degree of polymerization, X_N , can be expressed as

$$\bar{X}_N = \frac{\text{moles monomer consumed}/\text{dm}^3 \cdot \text{s}}{\text{dead polymer molecules produced}/\text{dm}^3 \cdot \text{s}} = \frac{-r_M}{\sum r_j} \quad (\text{P7-16.1})$$

- (a) Consider an additional termination step resulting from the combination of the initiator molecule and a free radical R_j :



- (b) Show that

$$\bar{X}_N = \left[\left(\frac{fk_0 k_t}{k_p^2} \right)^{1/2} \frac{(I_2)^{1/2}}{(M)} + \frac{k_m}{k_p} + \frac{k_s(S)}{k_p(M)} + \frac{k_{ti}(I)}{k_p(M)} \right]^{-1} \quad (\text{P7-16.3})$$

where

$$k_t = k_a + k_d + k_{ti}$$

- (c) Neglecting solvent transfer, show that

$$\frac{1}{\bar{X}_N} = \frac{k_t(-r_M)}{k_p^2(M)^2} + \frac{k_m}{k_p} + \frac{k_{ti}(I)}{k_p(M)}$$

- (d) Explain how you can determine rate law parameters from experimental data obtained in a CSTR. Use sketches to elucidate your explanation.
- (e) Typical activation energies for the initiation, propagation, and termination steps are: 20 kJ/mol, 20 kJ/mol, and 9 kJ/mol. Discuss the effect of temperature on free-radical polymerization.

P7-17_B The free-radical polymerization reaction discussed in Section 7.3.3 for a batch reactor is to be carried out in a CSTR and a PFR.

- (a) Plot the effluent initiator and monomer concentrations as a function of the space-time τ .
- (b) Compare your results for two equal-sized CSTRs in series with one CSTR. The total volume is the same in both cases.
- (c) Vary the parameter values (i.e., k_0 , k_p) and discuss your results.

Additional information:

$$M_0 = 3 \text{ mol/dm}^3 \quad I_{20} = 0.01 \text{ mol/dm}^3$$

$$k_0 = 10^{-3} \text{ s}^{-1} \quad k_p = 10 \text{ dm}^3/\text{mol} \cdot \text{s} \quad k_t = 5 \times 10^7 \text{ dm}^3/\text{mol} \cdot \text{s}$$

P7-18_A (Anionic polymerization)

- (a) Determine the final number-average and weight-average chain lengths and molecular weights along with the extent of polymerization and polydispersity in an anionic polymerization for an initial monomer concentration of 2 M and for initiator concentrations of 1, 0.01, and 0.0001 M.
- (b) Calculate the radical concentration and polymer concentration as a function of time for $j = 3, 7, 10$ for the same monomer and initiator concentrations. $k_i = \infty$, $k_p = 100 \text{ dm}^3/\text{mol} \cdot \text{s}$
- (c) Repeat (b) for the case

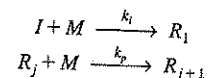
$$r_i = k_i[A^-]M$$

and

$$K_i = \frac{[A^-][B^+]}{[AB]}$$

with $k_i = 10 \text{ dm}^3/\text{mol} \cdot \text{s}$ and $K_i = 10^{-8} \text{ mol/dm}^3$.

P7-19_A An anionic polymerization is to be carried out in a CSTR. The reaction steps are

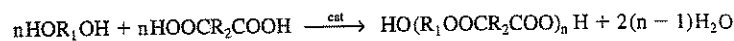


The entering concentration of monomer and initiator are M_0 and I_0 , respectively.

- (a) Derive an equation involving the monomer concentration and only the variables k_p , k_t , I_0 , τ (i.e., $\tau = V/v$), and M_0 .
 (b) Derive an equation of the radical concentration as a function of time.

$$(\text{Ans. } R_j = \frac{I_0}{(1 + \tau k_t M)} \frac{k_i}{k_p} \left(\frac{k_p M \tau}{1 + k_p M \tau} \right)^j)$$

- (c) Choose representative values of k_t ($0.015 \text{ dm}^3/\text{mol}\cdot\text{s}$) and k_p ($10^3 \text{ dm}^3/\text{mol}\cdot\text{s}$) to plot I and M as a function of τ . What if $k_t \gg k_p$ and $R_1 = I_0$?
 (d) Derive equations for the first and second moments and μ_n , μ_w , and D .
P7-20 Polyesters (shirts) can be formed by the reaction of diacids and diols

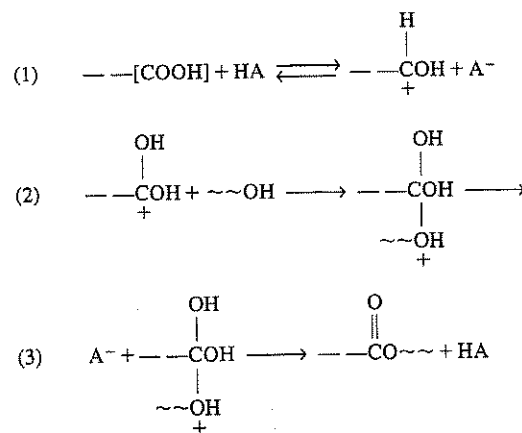


Let $[\text{COOH}]$ represent the concentration of carboxyl functional groups and $[\text{—OH}]$ the concentration of hydroxyl groups. The feed is equimolar in $[\text{OH}]$ and $[\text{COOH}]$.

The combined mole balance and rate law is

$$-\frac{d[\text{COOH}]}{dt} = k[\text{COOH}][\text{OH}][\text{cat}]$$

- (a) Assume that the polymerization is self catalyzed $[\text{cat}] = [\text{COOH}]$, plot the appropriate function of the fraction of functional groups reacted, p , as a function of time in order to obtain a linear plot. Plot the experimental data on the same plot. In what regions do the theory and experiment agree, and in which region do they disagree?
 (b) Assume that the reaction is catalyzed by the (H^+) ion and that the (H^+) ion is supplied by the dissociation of the weak acid $[\text{COOH}]$. Show that the overall rate of reaction is $5/2$ order. Plot the appropriate function of p versus time so that the plot is linear. In which regions do the theory and experiment agree, and which regions do they disagree?
 (c) It is proposed that the mechanism for the polymerization is



Can this mechanism be made to be consistent with both rate laws?

Additional information:

Experimental Data

t (min)	0	50	100	200	400	700	1200	1600
p	0	.049	0.68	0.8	0.88	0.917	0.936	0.944

- P7-21_B** Sketch the polymer concentration, P_j , mole fraction of polymer with j monomer units, y_j , and the corresponding weight fraction, w_j , for $j = 2, 10, 20$ as a function of monomer conversion in Styrene polymerization for
 (a) Termination by means other than combination.
 (b) Termination by combination. The molecular weight of the monomer is 25 and its initial concentration is 3 M and the initiator concentration is 0.01 M.
 (c) How would your answers to parts (a) and (b) change if the initiator concentration were 0.0001 M?
 (d) What are the corresponding average molecular weights at $X = 0.2, 0.8$, and 0.999?
P7-22_B Rework Example 7-5 for the case when the initiator does not react immediately with monomer to form the radical R_1^- (i.e., R_1), but instead reacts at a finite rate with a specific reaction rate k_0 :



The rate law is

$$-r_i = k_0 IM$$

The initiator concentration at time $t = 0$ is I_0 .

- (a) Derive an equation for R_j as a function of Θ .
 (b) For $M_0 = 3 \text{ mol/dm}^3$, $I_0 = 10^{-3} \text{ mol/dm}^3$, $k_0 = 0.1 \text{ dm}^3/\text{mol}\cdot\text{s}$, $k_p = 10 \text{ dm}^3/\text{mol}\cdot\text{s}$. Plot R_8 and P_8 as a function of real time t .

- P7-23_B** Rework Problem P7-22 for the case in which the reaction is carried out in a CSTR. Derive an equation for R_j as a function of the space-time, τ .

- P7-24_B** The growth of a bacteria *Stepinpoopi* can be described by the logistic growth law

$$r_g = \mu_m \left(1 - \frac{C_c}{C_m} \right) C_c$$

with $\mu_m = 0.5 \text{ h}^{-1}$ and $C_m = 20 \text{ g/dm}^3$. The substrate is in excess.

- (a) The cell growth is to be carried out in a 2-dm³ batch reactor. Plot the growth rate and cell concentration (g/dm^3) as functions of time after inoculation of 0.4 g of cells into the reactor (ignore the lag period).
 (b) The batch vessel in part (a) is to be turned into a CSTR. Derive an equation for the wash-out rate. Choose values for the volumetric flow rate of the entering substrate and plot the cell concentration as a function of time after inoculation.

- P7-25_B** The following data were obtained for *Pyrodictium occultum* at 98°C. Run 1 was carried out in the absence of yeast extract and run 2 with yeast extract. Both runs initially contained Na_2S . The vol % of the growth product H_2S collected above the broth was reported as a function of time. [*Ann. N. Y. Acad. Sci.*, 506, 51 (1987)].

Run 1:

Time (h)	0	10	15	20	30	40	50	60	70
Cell Density (cells/mL) $\times 10^{-4}$	2.7	2.8	15	70	400	600	775	600	525
% H ₂ S	0.5	0.8	1.0	1.2	6.8	4.7	7.5	8.0	8.2

Run 2:

Time (h)	0	5	10	15	20	30	40	50	60
Cell Density (cells/mL) $\times 10^{-4}$	2.7	7	11	80	250	350	350	250	—
% H ₂ S	0.1	0.7	0.7	0.8	1.2	4.3	7.5	11.0	12.3

- (a) What is the lag time with and without the yeast extract?
 (b) What is the difference in the specific growth rates, μ_{\max} , of the bacteria with and without the yeast extract?
 (c) How long is the stationary phase?
 (d) During which phase does the majority production of H₂S occur?
 (e) The liquid reactor volume in which these batch experiments were carried out was 0.2 dm³. If this reactor were converted to a continuous-flow reactor, what would be the corresponding wash-out rate?

P7-26c Cell growth with uncompetitive substrate inhibition is taking place in a CSTR. The cell growth rate law for this system is

$$r_s = \frac{\mu_{\max} C_s C_c}{K_s + C_s (1 + C_s/K_i)}$$

with $\mu_{\max} = 1.5 \text{ h}^{-1}$, $K_s = 1 \text{ g/dm}^3$, $K_i = 50 \text{ g/dm}^3$, $C_{s0} = 30 \text{ g/dm}^3$, $Y_{c/s} = 0.08$, $C_{c0} = 0.5 \text{ g/dm}^3$, and $D = 0.75 \text{ h}^{-1}$.

- (a) Make a plot of the steady-state cell concentration C_c as a function of D .
 (b) Make a plot of the substrate concentration C_s as a function of D on the same graph as that used for part (a).
 (c) Initially, 0.5 g/dm³ of bacteria was placed in the tank containing the substrate and the flow to the tank started. Plot the concentrations of bacteria and substrate as functions of time.

P7-27b A solution containing bacteria at a concentration of 0.001 g/dm³ was fed to a semibatch reactor. The nutrient was in excess and the growth rate law is first order in the cell concentration. The reactor was empty at the start of the experiment. If the concentration of bacteria in the reactor at the end of 2 h is 0.025 g/dm³, what is the specific growth rate k in min⁻¹?

P7-28a An understanding of bacteria transport in porous media is vital to the efficient operation of the water flooding of petroleum reservoirs. Bacteria can have both beneficial and harmful effects on the reservoir. In enhanced microbial oil recovery, EMOR, bacteria are injected to secrete surfactants to reduce the interfacial tension at the oil–water interface so that the oil will flow out more easily. However, under some circumstances the bacteria can be harmful, by plugging the pore space and thereby block the flow of water and oil. One bacteria that has been studied, *Leuconostoc mesenteroides*, has the unusual behavior that when it is injected into a porous medium and fed sucrose, it greatly

reduces the flow (i.e., damages the formation and reduces permeability). When the bacteria are fed fructose or glucose, there is no damage to the porous medium. [R. Lappan and H. S. Fogler, *SPE Prod. Eng.*, 7(2), 167–171 (1992)]. The cell concentration, C_c , is given below as a function of time for different initial sucrose concentrations.

- (a) From the data below, determine the lag time, the time to reach the stationary phase, the Michaelis constant, K_s , and the reaction velocity, μ , as a function of sucrose concentration.
 (b) Will an inhibition model of the form

$$r_s = \mu C_c \left(1 - \frac{C_c - C_{c0}}{C_p^*} \right)^n$$

where n and C_p^* are parameters, fit your data?

Cell Concentration Data

Sucrose Conc. Time (h)	1 g/cm ³ $C_c \times 10^{-7}$ (no./cm ³)	5 g/cm ³ $C_c \times 10^{-7}$ (no./cm ³)	10 g/cm ³ $C_c \times 10^{-7}$ (no./cm ³)	15 g/cm ³ $C_c \times 10^{-7}$ (no./cm ³)
0.00	3.00	2.00	2.00	1.33
1.00	4.16	3.78	6.71	5.27
2.00	5.34	5.79	1.11	0.30
3.00	7.35	—	5.72	3.78
4.00	6.01	9.36	3.71	7.65
5.00	8.61	6.68	8.32	10.3
6.00	10.1	17.6	21.1	17.0
7.00	18.8	35.5	37.6	38.4
8.00	28.9	66.1	74.2	70.8
9.00	36.2	143	180	194
10.0	42.4	160	269	283
11.0	44.4	170	237	279
12.0	46.9	165	256	306
13.0	46.9	163	149	289

P7-29a A CSTR is being operated at steady state. The cell growth follows the Monod growth law without inhibition. The exiting substrate and cell concentrations are measured as a function of the volumetric flow rate (represented as the dilution rate), and the results are shown below. Of course, measurements are not taken until steady state is achieved after each change in the flow rate. Neglect substrate consumption for maintenance and the death rate, and assume that $Y_{p/c}$ is zero. For run 4, the entering substrate concentration was 50 g/dm³ and the volumetric flow rate of the substrate was 2 dm³/s.

Run	C_s (g/dm ³)	D (s ⁻¹)	C_c (g/dm ³)
1	1	1	0.9
2	3	1.5	0.7
3	4	1.6	0.6
4	10	1.8	4

- (a) Determine the Monod growth parameters μ_{\max} and K_S .
 (b) Estimate the stoichiometric coefficients, $Y_{c/s}$ and $Y_{s/c}$.
- P7-30_B** The production of glycerol from corn amylum/asylum is to be carried out by fermentation using yeast cells (*Proc. 2nd Joint China/USA Chemical Engineering Conference*, Beijing, China, Vol. III, p. 1094, 1997). The growth law is

$$r_g = \mu C_C$$

with

$$\mu = \mu_0 \frac{C_S}{K_S + C_S + C_S^2/K_{SI}} \left(1 - \frac{C_P}{C_P^*} \right) \exp(-K_{PI}C_P)$$

$$\mu_0 = 0.25 \text{ L mg/mL} \cdot \text{s}$$

$$K_S = 0.018 \text{ mg/mL}$$

$$K_{SI} = 11.8 \text{ mg/mL}$$

$$C_P^* = 32.4 \text{ mg/mL}$$

$$K_{PI} = 0.06 \text{ mL/mg}$$

$$\frac{dP}{dt} = (\alpha\mu + \beta)X \quad \alpha = 34.5 \quad \beta = -0.147$$

$$\frac{dS}{dt} = \frac{1}{Y_{P/S}} \frac{dP}{dt} \quad Y_{P/S} = 1.33$$

Plot the concentration of cells, substrate, and product as a function of time for initial concentrations of cells of 10^{-8} g/dm^3 and a substrate concentration of 50 g/dm^3 .

- P7-31_B** Wastewater containing terephthalic acid (TA) is treated using two aerobic sludge tanks in series (*Proc. 2nd Joint China/USA Chemical Engineering Conference*, Beijing, China, Vol. III, p. 970, 1997). The first tank was 12 dm^3 and the second was 24 dm^3 . It is determined to reduce the TA concentration (reported in chemical oxygen demand, COD, mg/dm^3) from 5000 mg/dm^3 to below 100 mg/dm^3 . The results of the experiments were reported in the following manner:

$$\text{Tank 1:} \quad \frac{C_C V}{v_0(C_{S0} - C_S)} = 0.16 \frac{1}{C_S} + 0.62$$

with $\mu_0 = 1.61 \text{ day}^{-1}$ (g substrate/g cells) and $K_S = 0.25 \text{ g/dm}^3$ for the Monod equation.

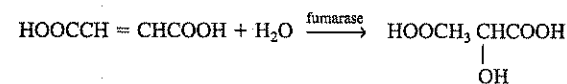
$$\text{Tank 2:} \quad \frac{C_C V}{v_0(C_{S0} - C_S)} = 0.3 \frac{1}{C_S} + 5.4$$

where C_C is the concentration of biomass in the tank and C_{S0} and C_S represent the entering and exiting concentration of TA in the waste stream.

Design a CSTR sludge system to handle a wastewater flow of $1000 \text{ m}^3/\text{day}$:

$$\text{loading} = 5-6 \frac{\text{kg COD}}{\text{m}^3 \cdot \text{h}}$$

- P7-32_B** The production of L-malic acid (used in medicines and food additives) was produced over immobilized cells of *Bacillus flavum* MA-3 (*Proc. 2nd Joint China/USA Chemical Engineering Conference*, Beijing, China, Vol. III, p. 1033, 1997).



The following rate law was obtained for the rate of formation of product:

$$r_P = \frac{V_{\max} C_S}{K_m + C_S} \left(1 - \frac{C_P}{C_P^*} \right) C_C$$

where $V_{\max} = 76$, $K_m = 0.048 \text{ mol/dm}^3$, and $C_P^* = 1.69 \text{ mol/dm}^3$. Design a reactor to process $10 \text{ m}^3/\text{day}$ of 2 mol/dm^3 of fumaric acid.



CD-ROM MATERIAL

• Learning Resources

1. *Summary Notes for Lectures 25, 26, 36, 37, 38, and 39*
4. *Solved Problems*

A. Hydrogen Bromide

Example CD7-1 Deducing the Rate Law

Example CD7-2 Find a Mechanism

• Living Example Problems

1. *Example 7-2 PSSH Applied to Thermal Cracking of Ethane*

• Professional Reference Shelf

1. *Enzyme Inhibition*

A. Competitive

Example CD7-3 Derive a Rate Law For Competitive Inhibition

B. Uncompetitive

Example CD7-4 Derive a Rate Law For Non-Competitive Inhibition

Example CD7-5 Match Eadie Plots to the Different Types of Inhibition

2. *Multiple Enzymes and Substrate Systems*

A. Enzyme Regeneration

Example CD7-6 Construct a Lineweaver-Burk Plot for Different Oxygen Concentrations

B. Enzyme Co-factors

Example CD7-7 Derive an Initial Rate Law for Alcohol Dehydrogenates

C. Multiple-Substrate Systems

Example CD7-8 Derive a Rate Law for a Multiple Substrate System

Example CD7-9 Calculate the Initial Rate of Formation of Ethanol in the Presence of Porpanediol

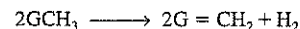
D. Multiple Enzyme Systems

3. *Oxidation Limited Fermentation*

4. *Fermentation Scale up*

• Additional Homework Problems

CDP7-A_A Determine the rate law and mechanism for the reaction



[2nd Ed. P7-6_A]

CDP7-B_A Suggest a mechanism for the reaction



[2nd Ed. P7-8_B]

CDP7-C_A Develop a rate law for substrate inhibition of an enzymatic reaction. [2nd Ed. P7-16_A]

CDP7-D_B Use POLYMATH to analyze an enzymatic reaction. [2nd Ed. P7-19_B]

CDP7-E_B Redo Problem P7-17 to include chain transfer. [2nd Ed. P7-23_B]

CDP7-F_B Determine the rate of diffusion of oxygen to cells. [2nd Ed. P12-12_B]

CDP7-G_B Determine the growth rate of amoeba predatory on bacteria. [2nd Ed. P12-15_C]

CDP7-H_C Plan the scale-up of an oxygen fermentor. [2nd Ed. P12-16_B]

CDP7-I_B Assess the effectiveness of bacteria used for denitrification in a batch reactor. [2nd Ed. P12-18_B]

CDP7-J_A Determine rate law parameters for the Monod equation. [2nd Ed. P12-19_A]

JOURNAL CRITIQUE PROBLEMS

- P7C-1 Compare the theoretical curve with actual data points in Figure 5b [*Biotechnol. Bioeng.*, 24, 329 (1982)], a normalized residence-time curve. Note that the two curves do not coincide at higher conversions. First, rederive the rate equation and the normalized residence-time equations used by the authors, and then, using the values for kinetic constants and lactase concentration cited by the authors, see if the theoretical curve can be duplicated. Linearize the normalized residence-time equation and replot the data, the theoretical curve in Figure 5b, and a theoretical curve that is obtained by using the constants given in the paper. What is the simplest explanation for the results observed?
- P7C-2 In Figure 3 [*Biotechnol. Bioeng.*, 23, 361 (1981)], $1/V$ was plotted against $(1/S)(1/\text{PGM})$ at three constant 7-ADCA concentrations, with an attempt to extract V_{\max} for the reaction. Does the V_{\max} obtained in this way conform to the true value? How is the experimental V_{\max} affected by the level of PGM in the medium?
- P7C-3 In *J. Catal.*, 79, 132 (1983), a mechanism was proposed for the catalyzed hydrogenation of pyridine in slurry reactors. Reexamine the data and model using an Eley-Rideal adsorption mechanism and comment on the appropriateness of this new analysis.

SUPPLEMENTARY READING

1. A discussion of complex reactions involving active intermediates is given in

FROST, A. A., and R. G. PEARSON, *Kinetics and Mechanism*, 2nd ed. New York: Wiley, 1961, Chap. 10.

LAIDLER, K. J., *Chemical Kinetics*, 3rd ed. New York: HarperCollins, 1987.

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SEINFELD, J. H., and S. N. PANDIS, *Atmospheric Chemistry and Physics*, New York: Wiley, 1998.

TEMKIN, O. N., *Chemical Reaction Networks: A Graph-Theoretical Approach*, Boca Raton, Fla: CRC Press, 1996.

2. Further discussion of enzymatic reactions is presented in

CORNISH-BOWDEN, A., *Analysis of Enzyme Kinetic Data*, New York: Oxford University Press, 1995.

VAN SANTEN, R. A. and J. W. NIEMANTSVERDIET, *Chemical Kinetics and Catalysis*, New York: Plenum Press, 1995.

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WINGARD, L. B., *Enzyme Engineering*. New York: Wiley-Interscience, 1972.

3. The following references concern polymerization reaction engineering:

BILLMEYER, F. W., *Textbook of Polymer Science*, 3rd ed. New York: Wiley, 1984.

DOTSON, N. A., R. GALVÁN, R. L. LAWRENCE, and M. TIRRELL, *Polymerization Process Modeling*, New York: VCH Publishers, 1996.

HOLLAND, C. D., and R. G. ANTHONY, *Fundamentals of Chemical Reaction Engineering*, 2nd ed. Upper Saddle River, N.J.: Prentice Hall, 1989, Chap. 10.

ODIAN, G., *Principles of Polymerization*, 3rd ed. New York: Wiley, 1983.

SCHORK, F. J., P. B. DESHPANDE, and K. W. LEFFEW, *Control of Polymerization Reactors*, New York: Marcel Dekker, 1993.

YOUNG, R. J. and P. A. LOVELL, *Introduction to Polymers*, 2nd ed., New York: Chapman & Hall, 1991.

4. Material on bioreactors can be found in

AIBA, S., A. E. HUMPHREY, N. F. MILLIS, *Biochemical Engineering*, 2nd ed. San Diego, Calif.: Academic Press, 1973.

BAILEY, T. J., and D. OLLIS, *Biochemical Engineering*, 2nd ed. New York: McGraw-Hill, 1987.

CRUEGER, W., and A. CRUEGER, *Biotechnology: A Textbook of Industrial Microbiology*. Madison, Wisc.: Science Tech., 1982.

SCRAGG, A. H., ed., *Biotechnology for Engineers*. New York: Wiley, 1988.

Steady-State Nonisothermal Reactor Design

8

If you can't stand the heat, get out of the kitchen.
Harry S Truman

Heat effects

We now focus our attention on heat effects in chemical reactors. The basic design equations, rate laws, and stoichiometric relationships derived and used in Chapter 4 for isothermal reactor design are still valid for the design of nonisothermal reactors. The major difference lies in the method of evaluating the design equation when temperature varies along the length of a PFR or when heat is removed from a CSTR. In Section 8.1 we show why we need the energy balance and how it will be used to solve reactor design problems. Section 8.2 concerns the derivation and manipulation of the energy balance for its application to various reactor types. In Sections 8.3 and 8.4, the energy balance is coupled with the mole balance, rate laws, and stoichiometry to design nonisothermal reactors. In Section 8.5 a typical nonisothermal industrial reactor and reaction, the SO_2 oxidation, is discussed in detail. We address the multiplicity of steady states in Section 8.6 and close the chapter with Section 8.7, nonisothermal multiple reactions.

8.1 Rationale

To identify the additional information necessary to design nonisothermal reactors, we consider the following example, in which a highly exothermic reaction is carried out adiabatically in a plug-flow reactor.

Example 8-1 What Additional Information Is Required?

Calculate the reactor volume necessary for 70% conversion.



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The reaction is exothermic and the reactor is operated adiabatically. As a result, the temperature will increase with conversion down the length of the reactor.

Solution

1. Design equation:

$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}} \quad (\text{E8-1.1})$$

2. Rate law:

$$-r_A = kC_A \quad (\text{E8-1.2})$$

3. Stoichiometry (liquid phase):

$$\begin{aligned} v &= v_0 \\ F_A &= C_A v_0 \\ F_{A0} &= C_{A0} v_0 \\ C_A &= C_{A0}(1 - X) \end{aligned} \quad (\text{E8-1.3})$$

4. Combining and canceling the entering concentration, C_{A0} , yields

$$\frac{dX}{dV} = \frac{k(1 - X)}{v_0} \quad (\text{E8-1.4})$$

Recalling the Arrhenius equation,

$$k = k_1 \exp \left[\frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T} \right) \right] \quad (\text{E8-1.5})$$

we know that k is a function of temperature, T . Consequently, because T varies along the length of the reactor, k will also vary, which was not the case for isothermal plug-flow reactors. Combining Equations (E8-1.4) and (E8-1.5) gives us

$$\frac{dX}{dV} = k_1 \exp \left[\frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T} \right) \right] \frac{1 - X}{v_0} \quad (\text{E8-1.6})$$

We see that we need another relationship relating X and T or T and V to solve this equation. *The energy balance will provide us with this relationship.*

8.2 The Energy Balance

8.2.1 First Law of Thermodynamics

We begin with the application of the first law of thermodynamics first to a closed system and then to an open system. A system is any bounded portion of the universe, moving or stationary, which is chosen for the application of the various thermodynamic equations. For a closed system, in which no mass

Why we need the
energy balance

crosses the system boundaries, the change in total energy of the system, $d\hat{E}$, is equal to the heat flow to the system, δQ , minus the work done by the system on the surroundings, δW . For a *closed system*, the energy balance is

$$d\hat{E} = \delta Q - \delta W \quad (8-1)$$

The δ 's signify that δQ and δW are not exact differentials of a state function.

The continuous-flow reactors we have been discussing are considered to be *open systems* in that mass crosses the system boundary. We shall carry out an energy balance on the open system as shown in Figure 8-1. For an open system in which some of the energy exchange is brought about by the flow of mass across the system boundaries, the energy balance for the case of *only one* species entering and leaving becomes

$$\left[\begin{array}{c} \text{rate of} \\ \text{accumulation} \\ \text{of energy} \\ \text{within the} \\ \text{system} \end{array} \right] = \left[\begin{array}{c} \text{rate of flow} \\ \text{of heat to} \\ \text{the system} \\ \text{from the} \\ \text{surroundings} \end{array} \right] - \left[\begin{array}{c} \text{rate of work} \\ \text{done by} \\ \text{the system} \\ \text{on the} \\ \text{surroundings} \end{array} \right] + \left[\begin{array}{c} \text{rate of energy} \\ \text{added to the} \\ \text{system by mass} \\ \text{flow into the} \\ \text{system} \end{array} \right] - \left[\begin{array}{c} \text{rate of} \\ \text{energy leaving} \\ \text{system by mass} \\ \text{flow out of} \\ \text{the system} \end{array} \right]$$

$$\frac{d\hat{E}_{\text{sys}}}{dt} = \dot{Q} - \dot{W} + F_{\text{in}} E_{\text{in}} - F_{\text{out}} E_{\text{out}} \quad (8-2)$$

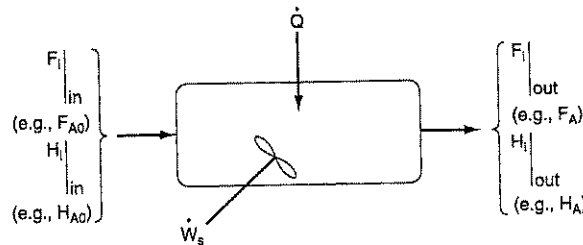


Figure 8-1 Energy balance on an open system: schematic.

The unsteady-state energy balance for an open system that has n species, each entering and leaving the system at its respective molar flow rates F_i (moles of i per time) and with its respective energy E_i (joules per mole of i), is

$$\frac{d\hat{E}_{\text{sys}}}{dt} = \dot{Q} - \dot{W} + \sum_{i=1}^n E_i F_i \Big|_{\text{in}} - \sum_{i=1}^n E_i F_i \Big|_{\text{out}} \quad (8-3)$$

The starting point

We will now discuss each of the terms in Equation (8-3).

8.2.2 Evaluating the Work Term

It is customary to separate the work term, \dot{W} , into *flow work* and *other work*, \dot{W}_s . Flow work is work that is necessary to get the mass *into* and *out of* the system. For example, when shear stresses are absent, we write

Flow work and shaft work

$$\dot{W} = \overbrace{- \sum_{i=1}^n F_i P V_i \Big|_{\text{in}} + \sum_{i=1}^n F_i P V_i \Big|_{\text{out}}}^{\text{[rate of flow work]}} + \dot{W}_s \quad (8-4)$$

where P is the pressure (Pa) and V_i is the specific volume (m^3/mol of i).

The term \dot{W}_s , often referred to as the *shaft work*, could be produced from such things as a stirrer in a CSTR or a turbine in a PFR. In most instances, the flow work term is combined with those terms in the energy balance that represent the energy exchange by mass flow across the system boundaries. Substituting Equation (8-4) into (8-3) and grouping terms, we have

$$\frac{d\hat{E}_{\text{sys}}}{dt} = \dot{Q} - \dot{W}_s + \sum_{i=1}^n F_i (E_i + P V_i) \Big|_{\text{in}} - \sum_{i=1}^n F_i (E_i + P V_i) \Big|_{\text{out}} \quad (8-5)$$

The energy E_i is the sum of the internal energy (U_i), the kinetic energy ($u_i^2/2$), the potential energy ($g z_i$), and any other energies, such as electric or magnetic energy or light:

$$E_i = U_i + \frac{u_i^2}{2} + g z_i + \text{other} \quad (8-6)$$

In almost all chemical reactor situations, the kinetic, potential, and "other" energy terms are negligible in comparison with the enthalpy, heat transfer, and work terms, and hence will be omitted; that is,

$$E_i = U_i \quad (8-7)$$

We recall that the enthalpy, H_i (J/mol), is defined in terms of the internal energy U_i (J/mol), and the product $P V_i$ ($1 \text{ Pa} \cdot \text{m}^3/\text{mol} = 1 \text{ J/mol}$):

Enthalpy

$$H_i = U_i + P V_i \quad (8-8)$$

Typical units of H_i are

$$(H_i) = \frac{\text{J}}{\text{mol } i} \text{ or } \frac{\text{Btu}}{\text{lb mol } i} \text{ or } \frac{\text{cal}}{\text{mol } i}$$

Enthalpy carried into (or out of) the system can be expressed as the sum of the net internal energy carried into (or out of) the system by mass flow plus the flow work:

$$F_i H_i = F_i (U_i + P V_i)$$

Combining Equations (8-5), (8-7), and (8-8), we can now write the energy balance in the form

$$\frac{d\hat{E}_{\text{sys}}}{dt} = \dot{Q} - \dot{W}_s + \sum_{i=1}^n F_i H_i \Big|_{\text{in}} - \sum_{i=1}^n F_i H_i \Big|_{\text{out}}$$

The energy of the system at any instant in time, \hat{E}_{sys} , is the sum of the products of the number of moles of each species in the system multiplied by their respective energies. This term will be discussed in more detail when unsteady-state reactor operation is considered in Chapter 9.

We shall let the subscript "0" represent the inlet conditions. Unsubscripted variables represent the conditions at the outlet of the chosen system volume.



$$\dot{Q} - \dot{W}_s + \sum_{i=1}^n F_{i0} H_{i0} - \sum_{i=1}^n F_i H_i = \frac{d\hat{E}_{\text{sys}}}{dt} \quad (8-9)$$

To put this equation in a more applicable form, there are two items to dissect:

1. The molar flow rates, F_i and F_{i0}
2. The molar enthalpies, H_i , H_{i0} [$H_i = H_i(T)$, and $H_{i0} = H_i(T_0)$]

CD-ROM animation



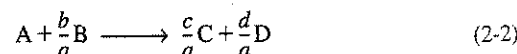
An animated version of what follows for the derivation of the energy balance can be found in the reaction engineering modules "Heat Effects 1" and "Heat Effects 2" on the CD-ROM.

8.2.3 Dissecting the Steady-State Molar Flow Rates to Obtain the Heat of Reaction

We will now consider flow systems that are operated at steady state. The steady-state energy balance is obtained by setting $(d\hat{E}_{\text{sys}}/dt)$ equal to zero in Equation (8-9) in order to yield

$$\dot{Q} - \dot{W}_s + \sum_{i=1}^n F_{i0} H_{i0} - \sum_{i=1}^n F_i H_i = 0 \quad (8-10)$$

To carry out the manipulations to write Equation (8-10) in terms of the heat of reaction we shall use the generalized reaction



The inlet and outlet terms in Equation (8-10) are expanded, respectively, to:

$$\text{In: } \sum H_{i0} F_{i0} = H_{A0} F_{A0} + H_{B0} F_{B0} + H_{C0} F_{C0} + H_{D0} F_{D0} + H_{I0} F_{I0} \quad (8-11)$$

and

$$\text{Out: } \sum H_i F_i = H_A F_A + H_B F_B + H_C F_C + H_D F_D + H_I F_I \quad (8-12)$$

We first express the molar flow rates in terms of conversion.

In general, the molar flow rate of species i for the case of no accumulation and a stoichiometric coefficient v_i is

$$F_i = F_{A0}(\Theta_i + v_i X)$$

Specifically, for Reaction (2-2) we have

$$F_A = F_{A0}(1 - X)$$

$$F_B = F_{A0} \left(\Theta_B - \frac{b}{a} X \right)$$

$$F_C = F_{A0} \left(\Theta_C + \frac{c}{a} X \right)$$

$$F_D = F_{A0} \left(\Theta_D + \frac{d}{a} X \right)$$

$$F_I = \Theta_I F_{A0}$$

Steady-state operation

We can substitute these values into Equations (8-11) and (8-12), then subtract Equation (8-12) from (8-11) to give

$$\begin{aligned} \sum_{i=1}^n H_{i0} F_{i0} - \sum_{i=1}^n F_i H_i &= F_{A0} [(H_{A0} - H_A) + (H_{B0} - H_B)\Theta_B \\ &\quad + [(H_{C0} - H_C)\Theta_C + (H_{D0} - H_D)\Theta_D + (H_{I0} - H_I)\Theta_I]] \\ &\quad - \underbrace{\left(\frac{d}{a} H_D + \frac{c}{a} H_C - \frac{b}{a} H_B - H_A \right)}_{\Delta H_{R_x}} F_{A0} X \end{aligned} \quad (8-13)$$

The term in parentheses that is multiplied by $F_{A0} X$ is called the **heat of reaction** at temperature T and is designated ΔH_{R_x} .

Heat of reaction at temperature T

$$\Delta H_{R_x}(T) = \frac{d}{a} H_D(T) + \frac{c}{a} H_C(T) - \frac{b}{a} H_B(T) - H_A(T) \quad (8-14)$$

All of the enthalpies (e.g., H_A , H_B) are evaluated at the temperature at the outlet of the system volume, and consequently, $[\Delta H_{R_x}(T)]$ is the heat of reaction at the specific temperature T . The heat of reaction is always given per mole of

the species that is the basis of calculation [i.e., species A (joules per mole of A reacted)].

Substituting Equation (8-14) into (8-13) and reverting to summation notation for the species, Equation (8-13) becomes

$$\sum_{i=1}^n F_{i0} H_{i0} - \sum_{i=1}^n F_i H_i = F_{A0} \sum_{i=1}^n \Theta_i (H_{i0} - H_i) - \Delta H_{Rx}(T) F_{A0} X \quad (8-15)$$

Combining Equations (8-10) and (8-15), we can now write the *steady-state* [i.e., $(d\dot{E}_{sys}/dt = 0)$] energy balance in a more usable form:

$$\dot{Q} - \dot{W}_s + F_{A0} \sum_{i=1}^n \Theta_i (H_{i0} - H_i) - \Delta H_{Rx}(T) F_{A0} X = 0 \quad (8-16)$$

If a *phase change* takes place during the course of a reaction, this form of the energy balance [i.e., Equation (8-16)] should be used, e.g., Problem 8-3.

8.2.4 Dissecting the Enthalpies

We are neglecting any enthalpy changes on mixing so that the partial molal enthalpies are equal to the molal enthalpies of the pure components. The molal enthalpy of species i at a particular temperature and pressure, H_i , is usually expressed in terms of an *enthalpy of formation* of species i at some reference temperature T_R , $H_i^\circ(T_R)$, plus the change in enthalpy that results when the temperature is raised from the reference temperature to some temperature T , ΔH_{Qi} :

$$H_i = H_i^\circ(T_R) + \Delta H_{Qi} \quad (8-17)$$

The reference temperature at which H_i° is given is usually 25°C. For any substance i that is being heated from T_1 to T_2 in the *absence* of phase change,

$$\Delta H_{Qi} = \int_{T_1}^{T_2} C_{pi} dT \quad (8-18)$$

Typical units of the heat capacity, C_{pi} , are

$$(C_{pi}) = \frac{\text{J}}{(\text{mol of } i)(\text{K})} \text{ or } \frac{\text{Btu}}{(\text{lb mol of } i)(\text{R})} \text{ or } \frac{\text{cal}}{(\text{mol of } i)(\text{K})}$$

Example 8-2 Relating $H_A(T)$ to $H_A^\circ(T_R)$

Species A is a solid at 25°C. Its enthalpy of formation is H_A° (298 K). Write an expression for the enthalpy of substance A in the gaseous state at temperature T .

Solution

Here, in addition to the increase in enthalpy of the solid, liquid, and gas from the temperature increase, one must include the heat of melting at the melting point, $\Delta H_{mA}(T_m)$, and the heat of vaporization at the boiling point, $\Delta H_{vA}(T_b)$.

One can use this form of the steady-state energy balance if the enthalpies are available

Calculating the enthalpy when phase changes are involved

$$\left[\begin{array}{c} \text{enthalpy of} \\ \text{species} \\ \text{A at } T \end{array} \right] = \left[\begin{array}{c} \text{enthalpy of} \\ \text{formation} \\ \text{of species} \\ \text{A at } T_R \end{array} \right] + \left[\begin{array}{c} \Delta H_Q \text{ in heating} \\ \text{solid from} \\ T_R \text{ to } T_m \end{array} \right] + \left[\begin{array}{c} \text{heat of} \\ \text{melting} \\ \text{at } T_m \end{array} \right] \quad (E8-2.1)$$

$$+ \left[\begin{array}{c} \Delta H_Q \text{ in heating} \\ \text{liquid from} \\ T_m \text{ to } T_b \end{array} \right] + \left[\begin{array}{c} \text{heat of} \\ \text{vaporization} \\ \text{at } T_b \end{array} \right] + \left[\begin{array}{c} \Delta H_Q \text{ in heating} \\ \text{gas from} \\ T_b \text{ to } T \end{array} \right]$$

$$H_A(T) = H_A^\circ(T_R) + \int_{T_R}^{T_m} C_{psA} dT + \Delta H_{mA}(T_m) + \int_{T_m}^{T_b} C_{plA} dT + \Delta H_{vA}(T_b) + \int_{T_b}^T C_{pvA} dT \quad (E8-2.2)$$

(See Problems P8-3 and P9-4.)

A large number of chemical reactions carried out in industry do not involve phase change. Consequently, we shall further refine our energy balance to apply to *single-phase* chemical reactions. Under these conditions the enthalpy of species i at temperature T is related to the enthalpy of formation at the reference temperature T_R by

$$H_i = H_i^\circ(T_R) + \int_{T_R}^T C_{pi} dT \quad (8-19)$$

If phase changes do take place in going from the temperature for which the enthalpy of formation is given and the reaction temperature T , Equation (E8-2.2) must be used instead of Equation (8-19).

The heat capacity at temperature T is frequently expressed as a quadratic function of temperature, that is,

$$C_{pi} = \alpha_i + \beta_i T + \gamma_i T^2 \quad (8-20)$$

To calculate the change in enthalpy ($H_i - H_{i0}$) when the reacting fluid is heated without phase change from its entrance temperature T_{i0} to a temperature T , we use Equation (8-19) to write

$$H_i - H_{i0} = \left[H_i^\circ(T_R) + \int_{T_R}^T C_{pi} dT \right] - \left[H_i^\circ(T_R) + \int_{T_R}^{T_{i0}} C_{pi} dT \right] = \int_{T_{i0}}^T C_{pi} dT \quad (8-21)$$

Substituting for H_i and H_{i0} in Equation (8-16) yields

$$\dot{Q} - \dot{W}_s - F_{A0} \sum_{i=1}^n \int_{T_{i0}}^T \Theta_i C_{pi} dT - \Delta H_{Rx}(T) F_{A0} X = 0 \quad (8-22)$$

Result of dissecting the enthalpies

8.2.5 Relating $\Delta H_{Rx}(T)$, $\Delta H_{Rx}^\circ(T_R)$, and ΔC_p

The heat of reaction at temperature T is given in terms of the enthalpy of each species at temperature T , that is,

$$\Delta H_{Rx}(T) = \frac{d}{a} H_D(T) + \frac{c}{a} H_C(T) - \frac{b}{a} H_B(T) - H_A(T) \quad (8-14)$$

where the enthalpy of each species is given by

$$H_i = H_i^\circ(T_R) + \int_{T_R}^T C_{pi} dT \quad (8-19)$$

If we now substitute for the enthalpy of each species, we have

$$\Delta H_{Rx}(T) = \left[\frac{d}{a} H_D^\circ(T_R) + \frac{c}{a} H_C^\circ(T_R) - \frac{b}{a} H_B^\circ(T_R) - H_A^\circ(T_R) \right] + \int_{T_R}^T \left[\frac{d}{a} C_{pD} + \frac{c}{a} C_{pC} - \frac{b}{a} C_{pB} - C_{pA} \right] dT \quad (8-23)$$

The first set of terms on the right-hand side of Equation (8-23) is the heat of reaction at the reference temperature T_R ,

$$\Delta H_{Rx}^\circ(T_R) = \frac{d}{a} H_D^\circ(T_R) + \frac{c}{a} H_C^\circ(T_R) - \frac{b}{a} H_B^\circ(T_R) - H_A^\circ(T_R) \quad (8-24)$$

One can look up the heats of formation at T_R , then calculate the heat of reaction at this reference temperature

The enthalpies of formation of many compounds, $H_i^\circ(T_R)$, are usually tabulated at 25°C and can readily be found in the *Handbook of Chemistry and Physics*¹ and similar handbooks. For other substances, the heat of combustion (also available in these handbooks) can be used to determine the enthalpy of formation. The method of calculation is described in these handbooks. From these values of the standard heat of formation, $H_i^\circ(T_R)$, we can calculate the heat of reaction at the reference temperature T_R from Equation (8-24).

The second term in brackets on the right-hand side of Equation (8-23) is the overall change in the heat capacity per mole of A reacted, ΔC_p ,

$$\Delta C_p = \frac{d}{a} C_{pD} + \frac{c}{a} C_{pC} - \frac{b}{a} C_{pB} - C_{pA} \quad (8-25)$$

Combining Equations (8-25), (8-24), and (8-23) gives us

$$\Delta H_{Rx}(T) = \Delta H_{Rx}^\circ(T_R) + \int_{T_R}^T \Delta C_p dT \quad (8-26)$$

Heat of reaction at temperature T

¹ CRC Handbook of Chemistry and Physics (Boca Raton, Fla.: CRC Press, 1996). <http://webbook.nist.gov>

Equation (8-26) gives the heat of reaction at any temperature T in terms of the heat of reaction at a reference temperature (usually 298 K) and an integral involving the ΔC_p term. Techniques for determining the heat of reaction at pressures above atmospheric can be found in Chen.² For the reaction of hydrogen and nitrogen at 400°C, it was shown that the heat of reaction increased by only 6% as the pressure was raised from 1 atm to 200 atm.

8.2.6 Constant or Mean Heat Capacities

For the case of constant or mean heat capacities, Equation (8-26) becomes

$$\Delta H_{Rx}(T) = \Delta H_{Rx}^\circ(T_R) + \Delta \hat{C}_p (T - T_R) \quad (8-27)$$

The circumflex denotes that the heat capacities are evaluated at some mean temperature value between T_R and T .

$$T_R \xrightarrow{\Delta \hat{C}_p} T \quad \Delta \hat{C}_p = \frac{\int_{T_R}^T \Delta C_p dT}{T - T_R} \quad (8-28)$$

In a similar fashion we can write the integral involving Θ_i and C_{pi} in Equation (8-22) as

$$\sum \Theta_i \int_{T_{i0}}^T C_{pi} dT = \sum \Theta_i \bar{C}_{pi} (T - T_{i0})$$

\bar{C}_{pi} is the mean heat capacity of species i between T_{i0} and T :

$$T_{i0} \xrightarrow{\bar{C}_{pi}} T \quad \bar{C}_{pi} = \frac{\int_{T_{i0}}^T C_{pi} dT}{T - T_{i0}} \quad (8-29)$$

Substituting the mean heat capacities into Equation (8-22), the steady-state energy balance becomes

Energy balance in terms of mean or constant heat capacities

$$\dot{Q} - \dot{W}_s - F_{A0} \sum \Theta_i \bar{C}_{pi} (T - T_{i0}) - F_{A0} X [\Delta H_{Rx}^\circ(T_R) + \Delta \hat{C}_p (T - T_R)] = 0 \quad (8-30)$$

In almost all of the systems we will study, the reactants will be entering the system at the same temperature; therefore, $T_{i0} = T_0$.

² N. H. Chen, *Process Reactor Design* (Needham Heights, Mass.: Allyn and Bacon, 1983), p. 26.

8.2.7 Variable Heat Capacities

We next want to arrive at a form of the energy balance for the case where heat capacities are strong functions of temperature over a wide temperature range. Under these conditions the mean values used in Equation (8-30) may not be adequate for the relationship between conversion and temperature. Combining Equation (8-23) with the quadratic form of the heat capacity, Equation (8-20),

$$C_{pi} = \alpha_i + \beta_i T + \gamma_i T^2 \quad (8-20)$$

we find that

$$\Delta H_{Rx}(T) = \Delta H_{Rx}^\circ(T_R) + \int_{T_R}^T (\Delta\alpha + \Delta\beta T + \Delta\gamma T^2) dT$$

Integrating gives us

Heat capacity as a function of temperature

$$\Delta H_{Rx}(T) = \Delta H_{Rx}^\circ(T_R) + \Delta\alpha(T - T_R) + \frac{\Delta\beta}{2}(T^2 - T_R^2) + \frac{\Delta\gamma}{3}(T^3 - T_R^3) \quad (8-31)$$

where

$$\Delta\alpha = \frac{d}{a}\alpha_D + \frac{c}{a}\alpha_C - \frac{b}{a}\alpha_B - \alpha_A$$

$$\Delta\beta = \frac{d}{a}\beta_D + \frac{c}{a}\beta_C - \frac{b}{a}\beta_B - \beta_A$$

$$\Delta\gamma = \frac{d}{a}\gamma_D + \frac{c}{a}\gamma_C - \frac{b}{a}\gamma_B - \gamma_A$$

In a similar fashion, we can evaluate the heat capacity term in Equation (8-22):

$$\begin{aligned} \sum_{i=1}^n \Theta_i \int_{T_0}^T C_{pi} dT &= \int_{T_0}^T (\sum \alpha_i \Theta_i + \sum \beta_i \Theta_i T + \sum \gamma_i \Theta_i T^2) dT \\ &= \sum \alpha_i \Theta_i (T - T_0) + \frac{\sum \beta_i \Theta_i}{2} (T^2 - T_0^2) + \frac{\sum \gamma_i \Theta_i}{3} (T^3 - T_0^3) \end{aligned} \quad (8-32)$$

Substituting Equations (8-31) and (8-32) into Equation (8-22), the form of the energy balance is

Energy balance for the case of highly temperature-sensitive heat capacities

$$\begin{aligned} \dot{Q} - \dot{W}_s - F_{A0} \left[\sum \alpha_i \Theta_i (T - T_0) + \frac{\sum \beta_i \Theta_i}{2} (T^2 - T_0^2) + \frac{\sum \gamma_i \Theta_i}{3} (T^3 - T_0^3) \right] \\ - F_{A0} X \left[\Delta H_{Rx}^\circ(T_R) + \Delta\alpha(T - T_R) + \frac{\Delta\beta}{2} (T^2 - T_R^2) + \frac{\Delta\gamma}{3} (T^3 - T_R^3) \right] = 0 \end{aligned} \quad (8-33)$$

Example 8-3 Heat of Reaction

Calculate the heat of reaction for the synthesis of ammonia from hydrogen and nitrogen at 150°C in kcal/mol of N₂ reacted and in kJ/mol of H₂ reacted.

Solution



Calculate the heat of reaction at the reference temperature using the heats of formation of the reacting species obtained from *Perry's Handbook*³ or the *Handbook of Chemistry and Physics*.

$$\Delta H_{Rx}^\circ(T_R) = 2H_{\text{NH}_3}^\circ(T_R) - 3H_{\text{H}_2}^\circ(T_R) - H_{\text{N}_2}^\circ(T_R) \quad (\text{E8-3.1})$$

The heats of formation of the elements (H₂, N₂) are zero at 25°C.

$$\begin{aligned} \Delta H_{Rx}^\circ(T_R) &= 2H_{\text{NH}_3}^\circ(T_R) - 3(0) - 0 = 2H_{\text{NH}_3}^\circ \\ &= 2(-11,020) \frac{\text{cal}}{\text{mol N}_2} \\ &= -22,040 \text{ cal/mol N}_2 \text{ reacted} \end{aligned}$$

or

$$\begin{aligned} \Delta H_{Rx}^\circ(298 \text{ K}) &= -22.04 \text{ kcal/mol N}_2 \text{ reacted} \\ &= -92.22 \text{ kJ/mol N}_2 \text{ reacted} \end{aligned}$$

The minus sign indicates the reaction is *exothermic*. If the heat capacities are constant or if the mean heat capacities over the range 25 to 150°C are readily available, the determination of ΔH_{Rx} at 150°C is quite simple.

$$\hat{C}_{p\text{H}_2} = 6.992 \text{ cal/mol H}_2 \cdot \text{K}$$

$$\hat{C}_{p\text{N}_2} = 6.984 \text{ cal/mol N}_2 \cdot \text{K}$$

$$\hat{C}_{p\text{NH}_3} = 8.92 \text{ cal/mol NH}_3 \cdot \text{K}$$

$$\begin{aligned} \Delta \hat{C}_p &= 2\hat{C}_{p\text{NH}_3} - 3\hat{C}_{p\text{H}_2} - \hat{C}_{p\text{N}_2} \\ &= 2(8.92) - 3(6.992) - 6.984 \\ &= -10.12 \text{ cal/g mol N}_2 \text{ reacted} \cdot \text{K} \end{aligned} \quad (\text{E8-3.2})$$

$$\begin{aligned} \Delta H_{Rx}(T) &= \Delta H_{Rx}^\circ(T_R) + \Delta \hat{C}_p (T - T_R) \\ \Delta H_{Rx}(423 \text{ K}) &= -22,040 + (-10.12)(423 - 298) \\ &= -23,310 \text{ cal/mol N}_2 = -23.31 \text{ kcal/mol N}_2 \\ &= -97,530 \text{ J/mol N}_2 \end{aligned} \quad (8-27)$$

(Recall: 1 cal = 4.184 J)

³ R. H. Perry, D. W. Green, and J. O. Maloney, eds., *Perry's Chemical Engineers' Handbook*, 6th ed. (New York: McGraw-Hill, 1984), pp. 3-147.

The heat of reaction based on the moles of H_2 reacted is

$$\begin{aligned}\Delta H_{Rx}(423\text{ K}) &= \frac{1\text{ g mol } N_2}{3\text{ g mol } H_2} \left(-97.53 \frac{\text{kJ}}{\text{mol } N_2} \right) \\ &= -32.51 \frac{\text{kJ}}{\text{mol } H_2} \text{ at } 423\text{ K}\end{aligned}$$

8.2.8 Heat Added to the Reactor, \dot{Q}

The heat flow *to* the reactor, \dot{Q} , is given in many instances in terms of the overall heat-transfer coefficient, U , the heat-exchange area, A , and the difference between the ambient temperature, T_a , and the reaction temperature, T .

CSTRs. Figure 8-2 shows schematics of a CSTR with a heat exchanger. The coolant enters the exchanger at a mass flow rate \dot{m}_c at a temperature T_{a1} and leaves at a temperature T_{a2} . The rate of heat transfer *from* the exchanger *to* the reactor is⁴

$$\dot{Q} = \frac{UA(T_{a1} - T_{a2})}{\ln[(T - T_{a1})/(T - T_{a2})]} \quad (8-34)$$

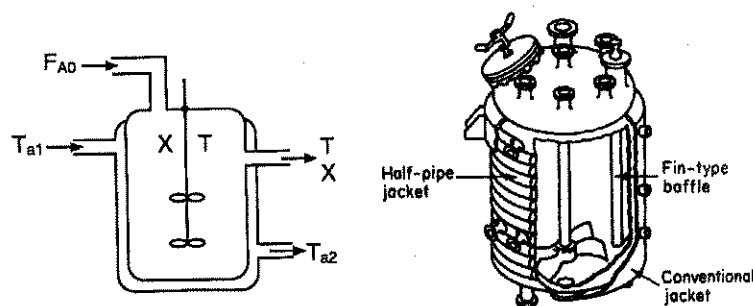


Figure 8-2 CSTR tank reactor with heat exchanger. [(b) Courtesy of Pfaudler, Inc.]

As a first approximation, we assume a quasi-steady state for the coolant flow and neglect the accumulation term (i.e., $dT_a/dt = 0$). An energy balance on the coolant fluid entering and leaving the exchanger is

⁴ Information on the overall heat-transfer coefficient may be found in C. O. Bennett and J. E. Myers, *Momentum, Heat, and Mass Transfer*, 2nd ed. (New York: McGraw-Hill, 1974), p. 316.

Energy balance on heat exchanger

$$\left[\begin{array}{c} \text{rate of} \\ \text{energy} \\ \text{in} \\ \text{by flow} \end{array} \right] - \left[\begin{array}{c} \text{rate of} \\ \text{energy} \\ \text{out} \\ \text{by flow} \end{array} \right] - \left[\begin{array}{c} \text{rate of} \\ \text{heat transfer} \\ \text{from exchanger} \\ \text{to reactor} \end{array} \right] = 0 \quad (8-35)$$

$$\dot{m}_c C_{pC}(T_{a1} - T_R) - \dot{m}_c C_{pC}(T_{a2} - T_R) - \frac{UA(T_{a1} - T_{a2})}{\ln(T - T_{a1})/(T - T_{a2})} = 0 \quad (8-36)$$

where C_{pC} is the heat capacity of the coolant fluid and T_R is the reference temperature. Simplifying gives us

$$\dot{Q} = \dot{m}_c C_{pC}(T_{a1} - T_{a2}) = \frac{UA(T_{a1} - T_{a2})}{\ln(T - T_{a1})/(T - T_{a2})} \quad (8-37)$$

Solving Equation (8-37) for the exit temperature of the coolant fluid yields

$$T_{a2} = T - (T - T_{a1}) \exp\left(\frac{-UA}{\dot{m}_c C_{pC}}\right) \quad (8-38)$$

From Equation (8-37)

$$\dot{Q} = \dot{m}_c C_{pC}(T_{a1} - T_{a2}) \quad (8-39)$$

Substituting for T_{a2} in Equation (8-39), we obtain

$$\dot{Q} = \dot{m}_c C_{pC} \left\{ (T_{a1} - T) \left[1 - \exp\left(\frac{-UA}{\dot{m}_c C_{pC}}\right) \right] \right\} \quad (8-40)$$

For large values of the coolant flow rate, the exponent can be expanded in a Taylor series where second-order terms are neglected in order to give

Heat transfer to a CSTR

$$\dot{Q} = \dot{m}_c C_{pC}(T_{a1} - T) \left[1 - \left(1 - \frac{UA}{\dot{m}_c C_{pC}} \right) \right] \quad (8-41)$$

Then

$$\dot{Q} = UA(T_a - T) \quad (8-42)$$

where $T_{a1} \approx T_{a2} = T_a$.

Tubular Reactors (PFR/PBR). When the heat flow varies along the length of the reactor, such as would be the case in a tubular flow reactor, we must integrate the heat flux equation along the length of the reactor to obtain the total heat added to the reactor,

$$\dot{Q} = \int^A U(T_a - T) dA = \int^V Ua(T_a - T) dV \quad (8-43)$$

where a is the heat-exchange area per unit volume of reactor. The variation in heat added along the reactor length (i.e., volume) is found by differentiating \dot{Q} with respect to V .

Heat transfer to a
PFR

$$\frac{d\dot{Q}}{dV} = Ua(T_a - T) \quad (8-44)$$

For a tubular reactor of diameter D ,

$$a = \frac{4}{D}$$

For a packed-bed reactor, we can write Equation (8-44) in terms of catalyst weight by simply dividing by the bulk catalyst density

$$\frac{1}{\rho_b} \frac{d\dot{Q}}{dV} = \frac{Ua}{\rho_b} (T_a - T) \quad (8-45)$$

Recalling $dW = \rho_b dV$, then

Heat transfer to a
PBR

$$\frac{d\dot{Q}}{dW} = \frac{Ua}{\rho_b} (T_a - T) \quad (8-46)$$

8.3 Nonisothermal Continuous-Flow Reactors

In this section we apply the general energy balance [Equation (8-22)] to the CSTR and to the tubular reactor operated at steady state. We then present example problems showing how the mole and energy balances are combined to size reactors operating adiabatically.

Substituting Equation (8-26) into Equation (8-22), the steady-state energy balance becomes

$$\dot{Q} - \dot{W}_s - F_{A0} \sum_{i=1}^n \int_{T_{i0}}^T \Theta_i C_{pi} dT - \left[\Delta H_{Rx}^\circ(T_R) + \int_{T_R}^T \Delta C_p dT \right] F_{A0} X = 0 \quad (8-47)$$

These are the forms
of the steady-state
balance we will use

[**Note:** In many calculations the CSTR mole balance ($F_{A0}X = -r_A V$) will be used to replace the term following the brackets in Equation (8-47); that is, ($F_{A0}X$) will be replaced by $(-r_A V)$.] Rearranging yields the steady-state balance for the case of *constant or mean heat capacities* in the form

$$\dot{Q} - \dot{W}_s - [\Delta H_{Rx}^\circ(T_R) + \Delta \hat{C}_p(T - T_R)] F_{A0} X = F_{A0} \sum_{i=1}^n \Theta_i \tilde{C}_{pi}(T - T_{i0}) \quad (8-48)$$

How can we use this information? Let's stop a minute and consider a system with the special set of conditions of no work, $\dot{W}_s = 0$, adiabatic operation $\dot{Q} = 0$, and then rearrange (8-48) into the form

$$X = \frac{\sum \Theta_i \tilde{C}_{pi}(T - T_{i0})}{-[\Delta H_{Rx}^\circ(T_R) + \Delta \hat{C}_p(T - T_R)]} \quad (8-49)$$

In many instances the $\Delta \hat{C}_p(T - T_R)$ term in the denominator of Equation (8-49) is negligible with respect to the ΔH_{Rx}° term, so that a plot of X vs. T will usually be linear, as shown in Figure 8-3. To remind us that the conversion in this plot was obtained from the energy balance rather than the mole balance it is given the subscript EB (i.e., X_{EB}) in Figure 8-3. Equation (8-49) applies to a CSTR, PFR, PBR, and also to a batch (as will be shown in Chapter 9). For $\dot{Q} = 0$ and $\dot{W}_s = 0$, Equation (8-49) gives us the explicit relationship between X and T needed to be used in conjunction with the mole balance to solve reaction engineering problems as discussed in Section 8.1.

Relationship
between X and T
for adiabatic
exothermic
reactions

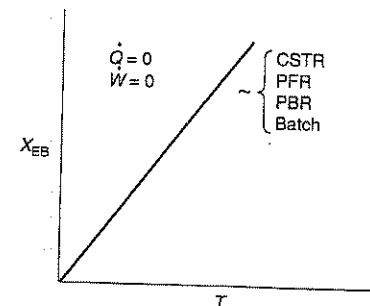


Figure 8-3 Adiabatic temperature-conversion relationship.

8.3.1 Application to the CSTR

Although the CSTR is well mixed and the temperature is uniform throughout the reaction vessel, these conditions do not mean that the reaction is carried out isothermally. Isothermal operation occurs when the feed temperature is identical to the temperature of the fluid inside the CSTR. The design equation for a CSTR in which there is no spatial variation in the rate of reaction is

$$V = \frac{F_{A0} X}{-r_A} \quad (2-13)$$

Equation (2-13) is coupled with a slight rearrangement of Equation (8-48):

$$\frac{\dot{Q} - \dot{W}_s}{F_{A0}} - X[\Delta H_{Rx}^\circ(T_R) + \Delta \hat{C}_p(T - T_R)] = \sum \Theta_i \tilde{C}_{pi}(T - T_{i0}) \quad (8-50)$$

TABLE 8-1. CSTR ALGORITHM

The first-order irreversible liquid-phase reaction	
$A \longrightarrow B$	
is carried out adiabatically.	
1. CSTR design equation:	$V = \frac{F_{A0}X}{-r_A} \quad (T8-1.1)$
2. Rate law:	$-r_A = kC_A \quad (T8-1.2)$
with	$k = Ae^{-E/RT} \quad (T8-1.3)$
3. Stoichiometry (liquid-phase, $v = v_0$):	$C_A = C_{A0}(1 - X)$
4. Combining yields	$V = \frac{v_0}{Ae^{-E/RT}} \left(\frac{X}{1 - X} \right) \quad (T8-1.4)$
Case A. The variables X , v_0 , C_{A0} , and F_{i0} are specified and the reactor volume, V , must be determined. The procedure is:	
5A. Solve for the temperature, T , for pure A entering, and $\tilde{C}_{pA} = \tilde{C}_{pB}$ ($\Delta\tilde{C}_p = 0$). For the adiabatic case, solve Equation (8-52) for T :	
	$T = T_0 + \frac{X(-\Delta H_{Rx}^\circ)}{\tilde{C}_{pA}} \quad (T8-1.5)$
For the nonadiabatic case with $Q = UA(T_d - T)$, solve Equation (8-51) for T :	
	$T = \frac{F_{A0}X(-\Delta H_{Rx}^\circ) + F_{A0}\tilde{C}_{pA}T_0 + UA T_d}{F_{A0}\tilde{C}_{pA} + UA} \quad (T8-1.6)$
6A. Calculate k from the Arrhenius equation.	
7A. Calculate the reactor volume, V , from Equation (T8-1.4).	
Case B. The variables v_0 , C_{A0} , V , and F_{i0} are specified and the exit temperature, T , and conversion, X , are unknown quantities. The procedure is:	
5B. Solve the energy balance (adiabatic) for X as a function of T .	
	$X_{EB} = \frac{\tilde{C}_{pA}(T - T_0)}{-[\Delta H_{Rx}^\circ(T_R)]} \quad (T8-1.7)$
For the nonadiabatic with $Q = UA(T_d - T)$ case, solve Equation (8-51) for X_{EB} :	
	$X_{EB} = \frac{UA(T - T_d)/F_{A0} + \tilde{C}_{pA}(T - T_0)}{-\Delta H_{Rx}^\circ} \quad (T8-1.8)$
6B. Solve Equation (T8-1.4) for X as a function of T .	
	$X_{MB} = \frac{\tau Ae^{-E/RT}}{1 + \tau Ae^{-E/RT}} \quad \text{where } \tau = V/v_0 \quad (T8-1.9)$
7B. Find the values of X and T that satisfy both the energy balance [Equation (T8-1.7)] and the mole balance [Equation (T8-1.9)]. This result can be achieved either numerically or graphically [plotting X vs. T using Equations (T8-1.7) and (T8-1.9) on the same graph].	

An algorithm

Divide and conquer

Energy balance

Mole balance

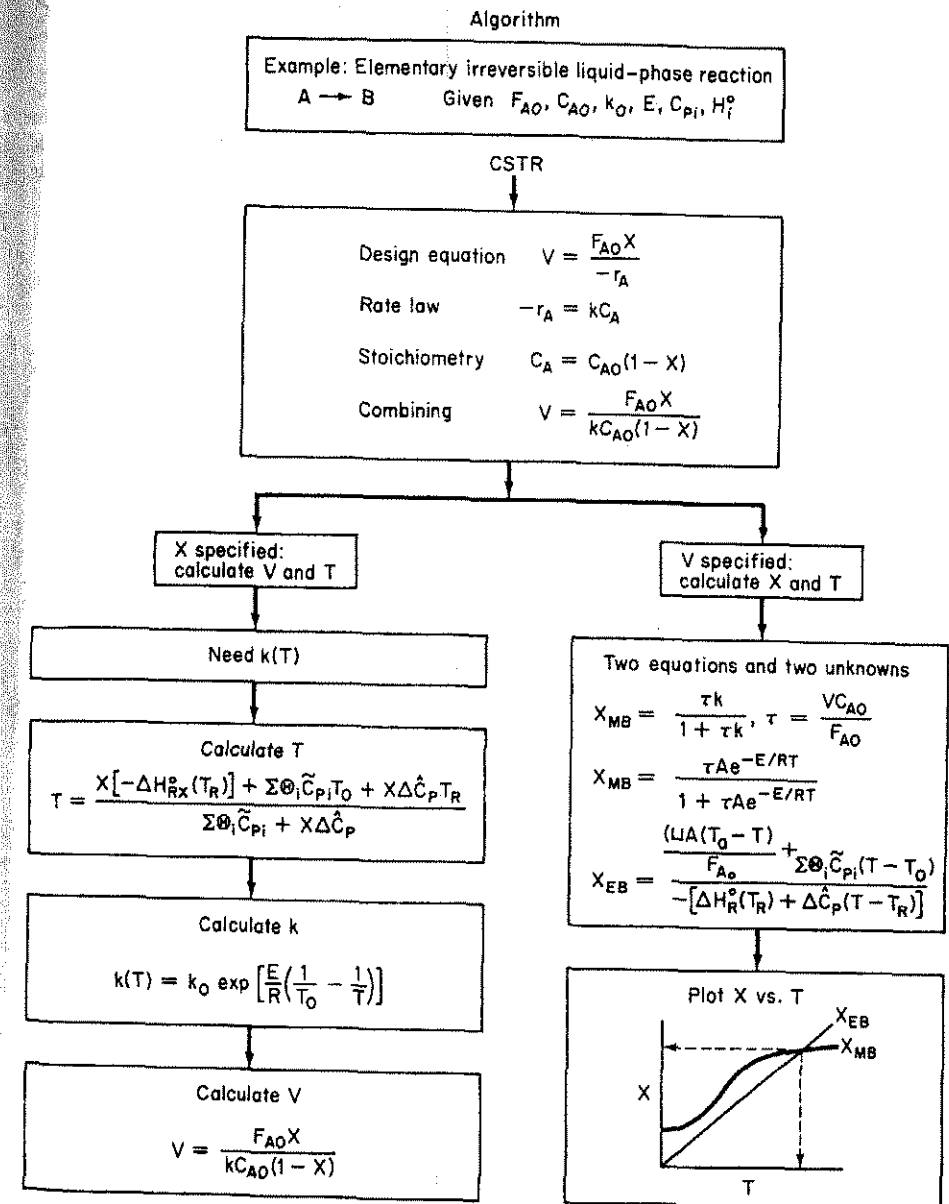


Figure 8-4 Algorithm for adiabatic CSTR design.

and used to design CSTRs (i.e., to obtain the reactor volume or operating temperature). If necessary, the CSTR is either heated or cooled by a heating or cooling jacket as shown in Figure 8-2, or by a coil placed inside the reactor.

Reactions are frequently carried out adiabatically, often with heating or cooling provided upstream or downstream of the reaction vessel. With the exception of processes involving highly viscous materials such as in Problem P8-4, the work done by the stirrer can usually be neglected. After substituting Equation (8-42) for \dot{Q} , the energy balance can be written as

$$\text{CSTR with heat exchange} \quad \frac{UA(T_a - T)}{F_{A0}} - X[\Delta H_{Rx}^\circ(T_R) + \Delta \hat{C}_p(T - T_R)] = \sum_{i=1}^n \Theta_i \tilde{C}_{pi}(T - T_{i0}) \quad (8-51)$$

Under conditions of adiabatic operation and negligible stirring work, both \dot{Q} and \dot{W}_s are zero, and the energy balance becomes

Adiabatic operation
of a CSTR

$$-X[\Delta H_{Rx}^\circ(T_R) + \Delta \hat{C}_p(T - T_R)] = \sum_{i=1}^n \Theta_i \tilde{C}_{pi}(T - T_{i0}) \quad (8-52)$$

The procedure for nonisothermal reactor design can be illustrated by considering the first-order irreversible liquid-phase reaction shown in Table 8-1. The algorithm for working through either case A or B is summarized in Figure 8-4. Its application is illustrated in the following example.

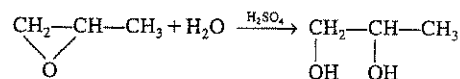
From here on, for the sake of brevity we will let

$$\Sigma = \sum_{i=1}^n$$

unless otherwise specified.

Example 8-4 Production of Propylene Glycol in an Adiabatic CSTR

Propylene glycol is produced by the hydrolysis of propylene oxide:



Production, uses,
and economics

Over 800 million pounds of propylene glycol were produced in 1997 and the selling price was approximately \$0.67 per pound. Propylene glycol makes up about 25% of the major derivatives of propylene oxide. The reaction takes place readily at room temperature when catalyzed by sulfuric acid.

You are the engineer in charge of an adiabatic CSTR producing propylene glycol by this method. Unfortunately, the reactor is beginning to leak, and you must replace it. (You told your boss several times that sulfuric acid was corrosive and that mild steel was a poor material for construction.) There is a nice overflow CSTR of 300-gal capacity standing idle; it is glass-lined and you would like to use it.

You are feeding 2500 lb/h (43.04 lb mol/h) of propylene oxide (P.O.) to the reactor. The feed stream consists of (1) an equimolar mixture of propylene oxide (46.62 ft³/h) and methanol (46.62 ft³/h), and (2) water containing 0.1 wt % H₂SO₄. The volumetric flow rate of water is 233.1 ft³/h, which is 2.5 times the methanol-P.O. flow rate. The corresponding molar feed rates of methanol and water are 71.87 and 802.8 lb mol/h, respectively. The water-propylene oxide-methanol mixture undergoes a slight decrease in volume upon mixing (approximately 3%), but you neglect this decrease in your calculations. The temperature of both feed streams is 58°F prior to mixing, but there is an immediate 17°F temperature rise upon mixing of the two feed streams caused by the heat of mixing. The entering temperature of all feed streams is thus taken to be 75°F (Figure E8-4.1).

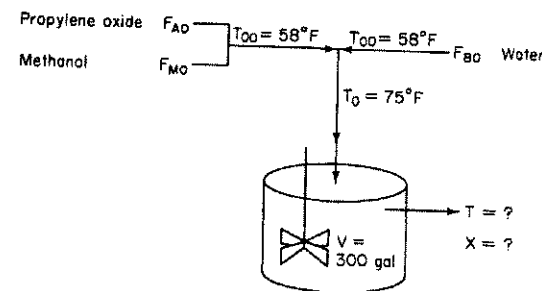


Figure E8-4.1

Furusawa et al.⁵ state that under conditions similar to those at which you are operating, the reaction is first-order in propylene oxide concentration and apparent zero-order in excess of water with the specific reaction rate

$$k = Ae^{-E/RT} = 16.96 \times 10^{12} (e^{-32,400/RT}) \text{ h}^{-1}$$

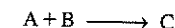
The units of E are Btu/lb mol.

There is an important constraint on your operation. Propylene oxide is a rather low-boiling substance (b.p. at 1 atm, 93.7°F). With the mixture you are using, you feel that you cannot exceed an operating temperature of 125°F, or you will lose too much oxide by vaporization through the vent system.

Can you use the idle CSTR as a replacement for the leaking one if it will be operated adiabatically? If so, what will be the conversion of oxide to glycol?

Solution

(All data used in this problem were obtained from the *Handbook of Chemistry and Physics* unless otherwise noted.) Let the reaction be represented by



where

⁵ T. Furusawa, H. Nishimura, and T. Miyauchi, *J. Chem. Eng. Jpn.*, 2, 95 (1969).

A is propylene oxide ($C_{pA} = 35 \text{ Btu/lb mol} \cdot ^\circ\text{F}$)⁶

B is water ($C_{pB} = 18 \text{ Btu/lb mol} \cdot ^\circ\text{F}$)

C is propylene glycol ($C_{pC} = 46 \text{ Btu/lb mol} \cdot ^\circ\text{F}$)

M is methanol ($C_{pM} = 19.5 \text{ Btu/lb mol} \cdot ^\circ\text{F}$)

In this problem neither the exit conversion nor the temperature of the adiabatic reactor is given. By application of the material and energy balances we can solve two equations with two unknowns (X and T). Solving these coupled equations, we determine the exit conversion and temperature for the glass-lined reactor to see if it can be used to replace the present reactor.

1. Mole balance and design equation:

$$F_{A0} - F_A + r_A V = 0$$

The design equation in terms of X is

$$V = \frac{F_{A0} X}{-r_A} \quad (\text{E8-4.1})$$

2. Rate law:

$$-r_A = k C_A \quad (\text{E8-4.2})$$

3. Stoichiometry (liquid-phase, $v = v_0$):

$$C_A = C_{A0}(1 - X) \quad (\text{E8-4.3})$$

4. Combining yields

$$V = \frac{F_{A0} X}{k C_{A0}(1 - X)} = \frac{v_0 X}{k(1 - X)} \quad (\text{E8-4.4})$$

5. Solving for X as a function of T and recalling that $\tau = V/v_0$ gives

$$X_{MB} = \frac{\tau k}{1 + \tau k} = \frac{\tau A e^{-E/RT}}{1 + \tau A e^{-E/RT}} \quad (\text{E8-4.5})$$

This equation relates temperature and conversion through the mole balance.

6. The energy balance for this adiabatic reaction in which there is negligible energy input provided by the stirrer is

$$-X[\Delta H_{Rx}^\circ(T_R) + \Delta \hat{C}_p(T - T_R)] = \sum \Theta_i \tilde{C}_{pi}(T - T_{i0}) \quad (\text{E8-52})$$

Solving for X , we obtain

$$X_{EB} = \frac{\sum \Theta_i \tilde{C}_{pi}(T - T_{i0})}{-[\Delta H_{Rx}^\circ(T_R) + \Delta \hat{C}_p(T - T_R)]} \quad (\text{E8-4.6})$$

⁶ C_{pA} and C_{pC} are estimated from the observation that the great majority of low-molecular-weight oxygen-containing organic liquids have a mass heat capacity of $0.6 \text{ cal/g} \cdot ^\circ\text{C} \pm 15\%$.

This equation relates X and T through the energy balance. We see that there are two equations [Equations (E8-4.5) and (E8-4.6)] that must be solved for the two unknowns, X and T .

7. Calculations:

a. Heat of reaction at temperature T :⁷

$$\Delta H_{Rx}(T) = \Delta H_{Rx}^\circ(T_R) + \Delta \hat{C}_p(T - T_R) \quad (\text{8-27})$$

$$H_A^\circ(68^\circ\text{F}) : -66,600 \text{ Btu/lb mol}$$

$$H_B^\circ(68^\circ\text{F}) : -123,000 \text{ Btu/lb mol}$$

$$H_C^\circ(68^\circ\text{F}) : -226,000 \text{ Btu/lb mol}$$

$$H_{Rx}^\circ(68^\circ\text{F}) = -226,000 - (-123,000) - (-66,600) \\ = -36,400 \text{ Btu/lb mol propylene oxide}$$

$$\Delta \hat{C}_p = \hat{C}_{pC} - \hat{C}_{pB} - \hat{C}_{pA} \quad (\text{E8-4.7}) \\ = 46 - 18 - 35 = -7 \text{ Btu/lb mol} \cdot ^\circ\text{F}$$

$$\Delta H_{Rx}(T) = -36,400 - (7)(T - 528)$$

b. Stoichiometry (C_{A0} , Θ_i , τ): The total liquid volumetric flow rate entering the reactor is

$$v_0 = v_{A0} + v_{M0} + v_{B0} \\ = 46.62 + 46.62 + 233.1 = 326.3 \text{ ft}^3/\text{h} \quad (\text{E8-4.8})$$

$$V = 300 \text{ gal} = 40.1 \text{ ft}^3$$

$$\tau = \frac{V}{v_0} = \frac{40.1 \text{ ft}^3}{326.3 \text{ ft}^3/\text{h}} = 0.1229 \text{ h}$$

$$C_{A0} = \frac{F_{A0}}{v_0} = \frac{43.04 \text{ lb mol/h}}{326.3 \text{ ft}^3/\text{h}} \\ = 0.132 \text{ lb mol/ft}^3 \quad (\text{E8-4.9})$$

$$\text{For methanol: } \Theta_M = \frac{F_{M0}}{F_{A0}} = \frac{71.87 \text{ lb mol/h}}{43.04 \text{ lb mol/h}} = 1.67$$

$$\text{For water: } \Theta_B = \frac{F_{B0}}{F_{A0}} = \frac{802.8 \text{ lb mol/h}}{43.04 \text{ lb mol/h}} = 18.65$$

c. Energy balance terms:

$$\sum \Theta_i \tilde{C}_{pi} = \tilde{C}_{pA} + \Theta_B \tilde{C}_{pB} + \Theta_M \tilde{C}_{pM} \\ = 35 + (18.65)(18) + (1.67)(19.5) \\ = 403.3 \text{ Btu/lb mol} \cdot ^\circ\text{F} \quad (\text{E8-4.10})$$

⁷ H_A° and H_C° are calculated from heat-of-combustion data.

Calculating the
parameter values

$$\begin{aligned} &\Delta H_{Rx} \\ &\Delta \hat{C}_p \\ &v_0 \\ &\tau \\ &C_{A0} \\ &\Theta_M \\ &\Theta_B \\ &\sum_{i=1}^n C_{pi} \Theta_i \end{aligned}$$

$$\begin{aligned}
 T_0 &= T_{00} + \Delta T_{\text{mix}} = 58^\circ\text{F} + 17^\circ\text{F} = 75^\circ\text{F} \\
 &= 535^\circ\text{R} \\
 T_R &= 68^\circ\text{F} = 528^\circ\text{R}
 \end{aligned}
 \quad (\text{E8-4.11})$$

The conversion calculated from the energy balance, X_{EB} , for an adiabatic reaction is found by rearranging Equation (8-52):

$$X_{\text{EB}} = -\frac{\sum \Theta_i \bar{C}_{pi}(T - T_{i0})}{\Delta H_{\text{Rx}}^\circ(T_R) + \Delta \bar{C}_p(T - T_R)} \quad (\text{E8-4.6})$$

Substituting all the known quantities into the mole and energy balances gives us

$$\begin{aligned}
 X_{\text{EB}} &= \frac{(403.3 \text{ Btu/lb mol} \cdot ^\circ\text{F})(T - 535)^\circ\text{F}}{-[-36,400 - 7(T - 528)] \text{ Btu/lb mol}} \\
 &= \frac{403.3(T - 535)}{36,400 + 7(T - 528)}
 \end{aligned}
 \quad (\text{E8-4.12})$$

The conversion calculated from the mole balance, X_{MB} , is found from Equation (E8-4.5).

$$\begin{aligned}
 X_{\text{MB}} &= \frac{(16.96 \times 10^{12} \text{ h}^{-1})(0.1229 \text{ h}) \exp(-32,400/1.987T)}{1 + (16.96 \times 10^{12} \text{ h}^{-1})(0.1229 \text{ h}) \exp(-32,400/1.987T)} \\
 &= \frac{(2.084 \times 10^{12}) \exp(-16,306/T)}{1 + (2.084 \times 10^{12}) \exp(-16,306/T)}
 \end{aligned}
 \quad (\text{E8-4.13})$$

8. **Solving.** There are a number of different ways to solve these two simultaneous equations [e.g., substituting Equation (E8-4.12) into (E8-4.13)]. To give insight into the functional relationship between X and T for the mole and energy balances, we shall obtain a graphical solution. Here X is plotted as a function of T for the mole and energy balances, and the intersection of the two curves gives the solution where both the mole and energy balance solutions are satisfied. In addition, by plotting these two curves we can learn if there is more than one intersection (i.e., multiple steady states) for which both the energy balance and mole balance are satisfied. If numerical root-finding techniques were used to solve for X and T , it would be quite possible to obtain only one root when there is actually more than one. We shall discuss multiple steady states further in Section 8.6. We choose T and then calculate X (Table E8-4.1). The calculations are plotted in Figure E8-4.2. The

TABLE E8-4.1

T (°R)	X_{MB} [Eq. (E8-4.13)]	X_{EB} [Eq. (E8-4.12)]
535	0.108	0.000
550	0.217	0.166
565	0.379	0.330
575	0.500	0.440
585	0.620	0.550
595	0.723	0.656
605	0.800	0.764
615	0.860	0.872
625	0.900	0.980

Plot X_{EB} as a
function of
temperature

Plot X_{MB} as a
function of
temperature

The reactor cannot
be used because it
will exceed the
specified maximum
temperature
of 585 R

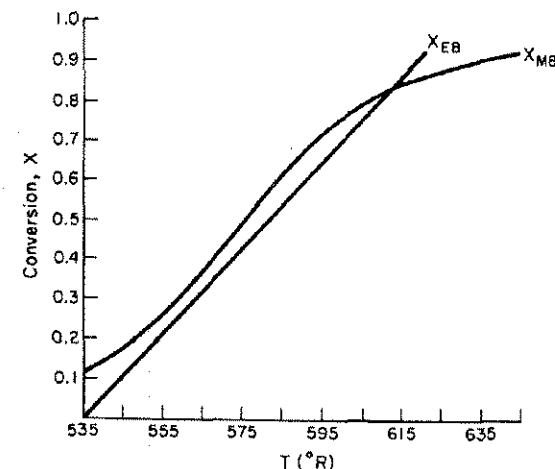


Figure E8-4.2

virtually straight line corresponds to the energy balance [Equation (E8-4.12)] and the curved line corresponds to the mole balance [Equation (E8-4.13)]. We observe from this plot that the only intersection point is at 85% conversion and 613°R. At this point both the energy balance and mole balance are satisfied. Because the temperature must remain below 125°F (585 R), we cannot use the 300-gal reactor as it is now.

Example 8-5 CSTR with a Cooling Coil

A cooling coil has been located for use in the hydration of propylene oxide discussed in Example 8-4. The cooling coil has 40 ft² of cooling surface and the cooling water flow rate inside the coil is sufficiently large that a constant coolant temperature of 85°F can be maintained. A typical overall heat-transfer coefficient for such a coil is 100 Btu/h·ft²·°F. Will the reactor satisfy the previous constraint of 125°F maximum temperature if the cooling coil is used?

Solution

If we assume that the cooling coil takes up negligible reactor volume, the conversion calculated as a function of temperature from the mole balance is the same as that in Example 8-4 [Equation (E8-4.13)].

1. Combining the mole balance, stoichiometry, and rate law, we have

$$X_{\text{MB}} = \frac{(2.084 \times 10^{12}) \exp(-16,306/T)}{1 + (2.084 \times 10^{12}) \exp(-16,306/T)} \quad (\text{E8-4.13})$$

2. **Energy balance.** Neglecting the work done by the stirrer, we combine Equations (8-42) and (8-50) to obtain

$$\frac{UA(T_a - T)}{F_{A0}} - X[\Delta H_{Rx}^\circ(T_R) + \Delta \hat{C}_p(T - T_R)] = \sum \Theta_i \tilde{C}_{pi}(T - T_0) \quad (\text{E8-5.1})$$

Solving the energy balance for X_{EB} yields

$$X_{EB} = \frac{\sum \Theta_i \tilde{C}_{pi}(T - T_0) + [UA(T - T_a)/F_{A0}]}{-[\Delta H_{Rx}^\circ(T_R) + \Delta \hat{C}_p(T - T_R)]} \quad (\text{E8-5.2})$$

The cooling coil term in Equation (E8-5.2) is

$$\frac{UA}{F_{A0}} = 100 \frac{\text{Btu}}{\text{h} \cdot \text{ft}^2 \cdot ^\circ\text{F}} \left(\frac{40 \text{ ft}^2}{43.04 \text{ lb mol/h}} \right) = \frac{92.9 \text{ Btu}}{\text{lb mol} \cdot ^\circ\text{F}} \quad (\text{E8-5.3})$$

Recall that the cooling temperature is

$$T_a = 85^\circ\text{F} = 545 \text{ R}$$

The numerical values of all other terms of Equation (E8-5.2) are identical to those given in Equation (E8-4.12):

$$X_{EB} = \frac{403.3(T - 535) + 92.9(T - 545)}{36,400 + 7(T - 528)} \quad (\text{E8-5.4})$$

We now have two equations [(E8-4.13) and (E8-5.4)] and two unknowns, X and T .

TABLE E8-5.1. POLYMATH: CSTR WITH HEAT EXCHANGE

Equations:	Initial Values:
$f(X) = X - \{403.3(T - 535) + 92.9(T - 545)\} / \{36400 + 7(T - 528)\}$	0.367
$f(T) = X - \tau u^* / (1 + \tau u^*)$	564
$\tau = 0.1229$	
$A = 16.96 \times 10^{12}$	
$E = 32400$	
$R = 1.987$	
$k = A \exp(-E/(R \cdot T))$	

TABLE E8-5.2. EXAMPLE 8-4 CSTR WITH HEAT EXCHANGE

Variable	Solution Value	f()
X	0.363609	-6.779e-16
T	563.729	-6.855e-16
tau	0.1229	
A	1.696e+13	
E	32400	
R	1.987	
k	4.64898	

We can now use the glass lined reactor

The POLYMATH program and solution to Equations (E8-4.13), X_{MB} , and (E8-5.4), X_{EB} , are given in Table E8-5.1. The exiting temperature and conversion are 103.7°F (563.7 R) and 36.4% , respectively.

8.3.2 Adiabatic Tubular Reactor

The energy balance given by Equation (8-48) relates the conversion at any point in the reactor to the temperature of the reaction mixture at the same point (i.e., it gives X as a function of T). Usually, there is a negligible amount of work done on or by the reacting mixture, so normally, the work term can be neglected in tubular reactor design. However, unless the reaction is carried out adiabatically, Equation (8-48) is still difficult to evaluate, because in nonadiabatic reactors, the heat added to or removed from the system varies along the length of the reactor. This problem does not occur in adiabatic reactors, which are frequently found in industry. Therefore, the adiabatic tubular reactor will be analyzed first.

Because \dot{Q} and W_s are equal to zero for the reasons stated above, Equation (8-47) reduces to

Energy balance for
adiabatic operation
of PFR

$$X[-\Delta H_{Rx}(T)] = \int_{T_0}^T \sum \Theta_i C_{pi} dT \quad (\text{8-53})$$

This equation can be combined with the differential mole balance

$$F_{A0} \frac{dX}{dV} = -r_A(X, T)$$

to obtain the temperature, conversion, and concentration profiles along the length of the reactor. One way of accomplishing this combination is to use Equation (8-53) to construct a table of T as a function of X . Once we have T as a function of X , we can obtain $k(T)$ as a function of X and hence $-r_A$ as a function of X alone. We then use the procedures detailed in Chapter 2 to size the different types of reactors.

The algorithm for solving PFRs and PBRs operated adiabatically is shown in Table 8-2.

TABLE 8-2A. ADIABATIC PFR/PBR ALGORITHM

The elementary reversible gas-phase reaction



is carried out in a PFR in which pressure drop is neglected and pure A enters the reactor.

$$\text{Mole balance:} \quad \frac{dX}{dV} = \frac{-r_A}{F_{A0}} \quad (\text{T8-2.1})$$

$$\text{Rate law:} \quad -r_A = k \left(C_A - \frac{C_B}{K_C} \right) \quad (\text{T8-2.2})$$

$$\text{with} \quad k = k_1 \exp \left[\frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T} \right) \right] \quad (\text{T8-2.3})$$

$$K_C = K(T_2) \exp \left[\frac{\Delta H_{Rx}^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T} \right) \right] \quad (\text{T8-2.4})$$

$$\text{Stoichiometry:} \quad \text{Gas, } \varepsilon = 0, P = P_0$$

$$C_A = C_{A0}(1-X) \frac{T_0}{T} \quad (\text{T8-2.5})$$

$$C_B = C_{A0}X \frac{T_0}{T} \quad (\text{T8-2.6})$$

Combine:

$$-r_A = k C_{A0} \left[(1-X) - \frac{X}{K_C} \right] \frac{T_0}{T} \quad (\text{T8-2.7})$$

Energy balance:

To relate temperature and conversion we apply the energy balance to an adiabatic PFR. If all species enter at the same temperature, $T_{i0} = T_0$. Solving Equation (8-50) to obtain the function of conversion yields

$$T = \frac{X[-\Delta H_{Rx}^\circ(T_R)] + \sum \Theta_i \bar{C}_{pi} T_0 + X \Delta \bar{C}_p T_R}{\sum \Theta_i \bar{C}_{pi} + X \Delta \bar{C}_p} \quad (\text{T8-2.8})$$

If pure A enters and $\Delta \bar{C}_p = 0$, then

$$T = T_0 + \frac{X[-\Delta H_{Rx}^\circ(T_R)]}{\bar{C}_{pA}} \quad (\text{T8-2.9})$$

Equations (T8-2.1) through (T8-2.9) can easily be solved using either Simpson's rule or an ODE solver.

TABLE 8-2B. SOLUTION PROCEDURES FOR ADIABATIC PFR/PBR REACTOR

A. Numerical Technique

Integrating the PFR mole balance,

$$V = F_{A0} \int_0^{X_3} \frac{dX}{-r_A} = F_{A0} \int_0^{X_3} \left(\frac{1}{-r_A} \right) dX \quad (\text{T8-2.10})$$

1. Set $X = 0$.
2. Calculate T using Equation (T8-2.9).
3. Calculate k using Equation (T8-2.3).
4. Calculate K_C using Equation (T8-2.4).
5. Calculate T_0/T (gas phase).
6. Calculate $-r_A$ using Equation (T8-2.7).
7. Calculate $(1/-r_A)$.
8. If X is less than the X_3 specified, increment X (i.e., $X_{i+1} = X_i + \Delta X$) and go to step 2.
9. Prepare table of X vs. $(1/-r_A)$.
10. Use numerical integration formulas, for example,

$$V = F_{A0} \int_0^{X_3} \left(\frac{1}{-r_A} \right) dX = \frac{3}{8} h \left[\frac{1}{-r_A(X=0)} + \frac{3}{-r_A(X_1)} + \frac{3}{-r_A(X_2)} + \frac{1}{-r_A(X_3)} \right] \quad (\text{T8-2.11})$$

with

$$h = \frac{X_3}{3}$$

B. Ordinary Differential Equation (ODE) Solver

$$1. \quad \frac{dX}{dV} = k C_{A0} \left[(1-X) - \frac{X}{K_C} \right] \frac{T_0}{T} \quad (\text{T8-2.12})$$

$$2. \quad k = k_1(T_1) \exp \left[\frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T} \right) \right] \quad (\text{T8-2.13})$$

$$3. \quad K_C = K_C(T_2) \exp \left[\frac{\Delta H_{Rx}^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T} \right) \right] \quad (\text{T8-2.14})$$

$$4. \quad T = T_0 + \frac{X[-\Delta H_{Rx}^\circ(T_R)]}{\bar{C}_{pA}} \quad (\text{T8-2.15})$$

5. Enter parameter values k_1 , E , R , K_{C2} , $\Delta H_{Rx}^\circ(T_R)$, \bar{C}_{pA} , C_{A0} , T_0 , T_1 , T_2 .
6. Enter in initial values $X = 0$, $V = 0$ and final values $X = X_f$ and $V = V_f$.

Example 8-6 Liquid-Phase Isomerization of Normal Butane

Normal butane, C_4H_{10} , is to be isomerized to isobutane in a plug-flow reactor. Isobutane is a valuable product that is used in the manufacture of gasoline additives. For example, isobutane can be further reacted to form isooctane. The 1996 selling price of *n*-butane was 37.2 cents per gallon, while the price of isobutane was 48.5 cents per gallon.

The reaction is to be carried out adiabatically in the liquid phase under high pressure using essentially trace amounts of a liquid catalyst which gives a specific reaction rate of 31.1 h^{-1} at 360 K. Calculate the PFR volume necessary to process 100,000 gal/day (163 kg mol/h) of a mixture 90 mol % *n*-butane and 10 mol % *i*-pentane, which is considered an inert. The feed enters at 330 K.

Additional information:

$$\Delta H_{RX} = -6900 \text{ J/mol} \cdot \text{butane}$$

Butane

i-Pentane

$$C_{p_{n-B}} = 141 \text{ J/mol} \cdot \text{K}$$

$$C_{p_{i-P}} = 161 \text{ J/mol} \cdot \text{K}$$

$$C_{p_{i-B}} = 141 \text{ J/mol} \cdot \text{K}$$

$$\text{Activation energy} = 65.7 \text{ kJ/mol}$$

$$K_C = 3.03 \text{ at } 60^\circ\text{C}$$

$$C_{A0} = 9.3 \text{ g mol/dm}^3 = 9.3 \text{ kg mol/m}^3$$

Solution



$$\text{Mole balance: } F_{A0} \frac{dX}{dV} = -r_A \quad (\text{E8-6.1})$$

$$\text{Rate law: } -r_A = k \left(C_A - \frac{C_B}{K_C} \right) \quad (\text{E8-6.2})$$

$$k = k(T_1) e^{\left[\frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T} \right) \right]} \quad (\text{E8-6.3})$$

$$K_C = K_C(T_2) e^{\left[\frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T} \right) \right]} \quad (\text{E8-6.4})$$

Stoichiometry (liquid phase, $v = v_0$):

$$C_A = C_{A0}(1 - X) \quad (\text{E8-6.5})$$

$$C_B = C_{A0}X \quad (\text{E8-6.6})$$

Combine:

$$-r_A = kC_{A0} \left[1 - \left(1 + \frac{1}{K_C} \right) X \right] \quad (\text{E8-6.7})$$

Integrating Equation (E8-6.1) yields

$$V = \int_0^X \frac{F_{A0}}{-r_A} dX \quad (\text{E8-6.8})$$

The economic incentive
\$ = 48.5¢/lb
vs. 37.2¢/lb

The algorithm

Energy balance. Recalling Equation (8-30), we have

$$\dot{Q} - \dot{W}_s - F_{A0} \sum (\Theta_i \tilde{C}_{pi} (T - T_0)) - F_{A0} X [\Delta H_{RX}^\circ(T_R) + \Delta \tilde{C}_p (T - T_R)] = 0 \quad (\text{8-30})$$

From the problem statement

$$\text{Adiabatic: } \dot{Q} = 0$$

$$\text{No work: } \dot{W}_s = 0$$

$$\Delta \tilde{C}_p = \tilde{C}_{p_B} - \tilde{C}_{p_A} = 141 - 141 = 0$$

Applying the conditions above to Equation (8-30) and rearranging gives

$$T = T_0 + \frac{(-\Delta H_{RX})X}{\sum \Theta_i \tilde{C}_{pi}} \quad (\text{E8-6.9})$$

$$\begin{aligned} \sum \Theta_i \tilde{C}_{pi} &= \tilde{C}_{p_A} + \Theta_i \tilde{C}_{p_i} = \left(141 + \frac{0.1}{0.9} 161 \right) \text{ J/mol} \cdot \text{K} \\ &= 159.5 \text{ J/mol} \cdot \text{K} \end{aligned}$$

$$T = 330 + \frac{-(-6900)}{159.5} X$$

$$T = 330 + 43.3 X \quad (\text{E8-6.10})$$

Substituting for the activation energy, T_1 , and k_1 in Equation (E8-6.3), we obtain

$$k = 31.1 \exp \left[\frac{65,700}{8.31} \left(\frac{1}{360} - \frac{1}{T} \right) \right]$$

$$k = 31.1 \exp \left[7906 \left(\frac{T - 360}{360T} \right) \right] \quad (\text{E8-6.11})$$

Substituting for ΔH_{RX} , T_2 , and $K_C(T_2)$ in Equation (E8-6.4) yields

$$K_C = 3.03 \exp \left[\frac{-6900}{8.31} \left(\frac{1}{333} - \frac{1}{T} \right) \right]$$

$$K_C = 3.03 \exp \left[-830.3 \left(\frac{T - 333}{333T} \right) \right] \quad (\text{E8-6.12})$$

Recalling the rate law gives us

$$-r_A = kC_{A0} \left[1 - \left(1 + \frac{1}{K_C} \right) X \right] \quad (\text{E8-6.7})$$

At equilibrium

$$-r_A = 0$$

and therefore we can solve Equation (E8-6.7) for the equilibrium conversion

$$X_e = \frac{K_C}{1 + K_C} \quad (\text{E8-6.13})$$

Solution by Hand Calculation (you probably won't see this in the 4th edition)

We will now integrate Equation (E8-6.8) using Simpson's rule after forming a table (E8-6.1) to calculate $(F_{A0}/-r_A)$ as a function of X . This procedure is similar to that described in Chapter 2. We now carry out a sample calculation to show how Table E8-6.1 was constructed, for example, at $X = 0.2$.

(a) $T = 330 + 43.33(0.2) = 338.6 \text{ K}$

(b) $k = 31.1 \exp \left[7906 \left(\frac{338.6 - 360}{(360)(338.6)} \right) \right] = 31.1 \exp(-1.388) = 7.76 \text{ h}^{-1}$

(c) $K_C = 3.03 \exp \left[-830.3 \left(\frac{338.6 - 333}{(333)(338.6)} \right) \right] = 3.03 e^{-0.0412} = 2.9$

(d) $X_e = \frac{2.9}{1 + 2.9} = 0.74$

(e) $-r_A = \left(\frac{7.76}{\text{h}} \right) (9.3) \frac{\text{mol}}{\text{dm}^3} \left[1 - \left(1 + \frac{1}{2.9} \right) (0.2) \right] = 52.8 \frac{\text{mol}}{\text{dm}^3 \cdot \text{h}} = 52.8 \frac{\text{kmol}}{\text{m}^3 \cdot \text{h}}$

(f) $\frac{F_{A0}}{-r_A} = \frac{(0.9 \text{ mol butane/mol total})(163 \text{ kmol total/h})}{52.8 \frac{\text{kmol}}{\text{m}^3 \cdot \text{h}}} = 2.778 \text{ m}^3$

TABLE E8-6.1. HAND CALCULATION

X	$T \text{ (K)}$	$k \text{ (h}^{-1}\text{)}$	K_C	X_e	$-r_A \text{ (kmol/m}^3 \cdot \text{h)}$	$\frac{F_{A0}}{-r_A} \text{ (m}^3\text{)}$
0	330	4.22	3.1	0.76	39.2	3.74
0.2	338.7	7.76	2.9	0.74	52.8	2.78
0.4	347.3	13.93	2.73	0.73	58.6	2.50
0.6	356.0	24.27	2.57	0.72	37.7	3.89
0.65	358.1	27.74	2.54	0.715	24.5	5.99
0.7	360.3	31.67	2.5	0.71	4.1	35.8

$$V = \int_0^{0.6} \frac{F_{A0}}{-r_A} dX + \int_{0.6}^{0.7} \frac{F_{A0}}{-r_A} dX \quad (\text{E8-6.14})$$

Using Equations (A-24) and (A-22), we obtain

$$V = \frac{3}{8} (0.15) [3.74 + 3(2.78) + 3(2.5) + 3.89] \text{ m}^3 + \frac{0.1}{3} [3.89 + 4(5.99) + 35.8] \text{ m}^3$$

$$= 1.32 \text{ m}^3 + 2.12 \text{ m}^3$$

$$V = 3.4 \text{ m}^3$$

Sample calculation
for Table E8-6.1

Computer Solution

We could have also solved this problem using POLYMATH or some other ODE solver. The POLYMATH program using Equations (E8-6.1), (E8-6.10), (E8-6.7), (E8-6.11), (E8-6.12), and (E8-6.13) is shown in Table E8-6.2. The graphical output is

TABLE E8-6.2. POLYMATH PROGRAM

Equations:	Initial Values:
$d(X)/d(V) = -r_A/F_{A0}$	0
$T = 330 + 43.3 \cdot X$	
$F_{A0} = 9 \cdot 163$	
$C_{A0} = 9.3$	
$k = 31.1 \cdot \exp(7906 \cdot (T - 360) / (T \cdot 360))$	
$K_C = 3.03 \cdot \exp(-830.3 \cdot (T - 333) / (T \cdot 333))$	
$X_e = K_C / (1 + K_C)$	
$r_A = -k \cdot C_{A0} \cdot (1 - (1 + 1/K_C) \cdot X)$	
$\text{rate} = -r_A$	
$V_0 = 0, \quad V_f = 3.3$	

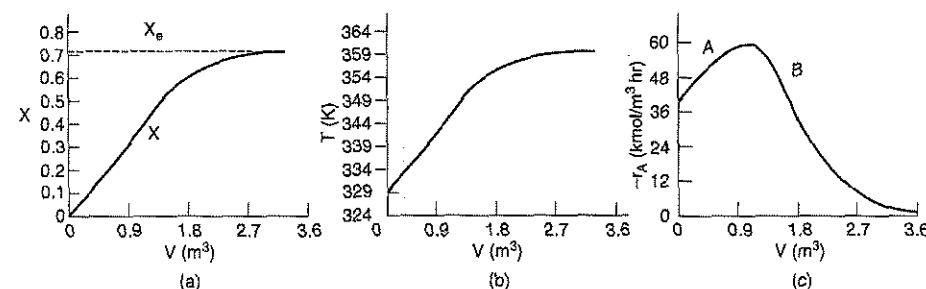


Figure E8-6.1 Conversion, temperature, and reaction rate profiles.

shown in Figure E8-6.1. We see from Figure E8-6.1a that 1.15 m³ is required to 40% conversion. The conversion, temperature, in Figure E8-6.1 and reaction rate profiles are shown. One observes that the rate of reaction

$$-r_A = \underbrace{k C_{A0}}_A \underbrace{\left[1 - \left(1 + \frac{1}{K_C} \right) X \right]}_B \quad (\text{E8-6.15})$$

goes through a maximum. Near the entrance to the reactor, term A increases more rapidly than term B decreases and thus the rate increases. Near the end of the reactor, term B is decreasing more rapidly than term A increases. Consequently, because of these two competing effects, we have a maximum in the rate of reaction.

Let's calculate the CSTR volume necessary to achieve 40% conversion. The mole balance is

$$V = \frac{F_{A0}X}{-r_A}$$

Using Equation (E8-6.2) in the mole balance, we obtain

$$V = \frac{F_{A0}X}{kC_{A0}\left[1 - \left(1 + \frac{1}{K_C}\right)X\right]} \quad (\text{E8-6.16})$$

From the energy balance we have Equation (E8-6.10):

$$\begin{aligned} T &= 330 + 43.3X \\ &= 330 + 43.3(0.4) = 347.3 \end{aligned}$$

Using Equations (E8-6.11) and (E8-6.12) or from Table E8-6.1,

$$\begin{aligned} k &= 13.93 \text{ h}^{-1} \\ K_C &= 2.73 \end{aligned}$$

Then

$$\begin{aligned} -r_A &= 58.6 \text{ kmol/m}^3 \cdot \text{h} \\ V &= \frac{(146.7 \text{ kmol butane/h})(0.4)}{58.6 \text{ kmol/m}^3 \cdot \text{h}} \\ V &= 1.0 \text{ m}^3 \end{aligned}$$

The adiabatic CSTR volume is less than the PFR volume

We see that the CSTR volume (1 m³) to achieve 40% conversion in this adiabatic reaction is less than the PFR volume (1.15 m³).

8.3.3 Steady-State Tubular Reactor with Heat Exchange

In this section we consider a tubular reactor in which heat is added or removed through the cylindrical walls of the reactor (Figure 8-5). In modeling the reactor we shall assume that there is no radial gradient in the reactor and that the heat flux through the wall per unit volume of reactor is as shown in Figure 8-5.

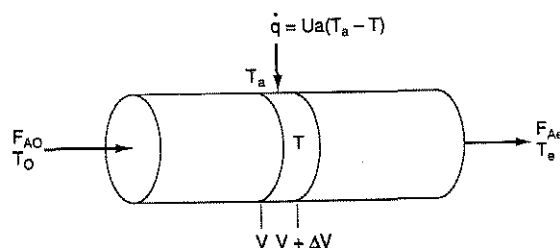


Figure 8-5 Tubular reactor with heat gain or loss.

Recalling Equation (8-47) and ignoring any work done on the reacting fluid, we obtain

$$\dot{Q} - F_{A0} \int_{T_0}^T \sum \Theta_i C_{pi} dT - \left[\Delta H_{Rx}^\circ(T_R) + \int_{T_R}^T \Delta C_p dT \right] F_{A0} X = 0 \quad (8-54)$$

Differentiating with respect to the volume V and collecting terms gives us

$$\begin{aligned} \frac{d\dot{Q}}{dV} - [F_{A0}(\sum \Theta_i C_{pi} + X \Delta C_p)] \frac{dT}{dV} \\ - \left[\Delta H_{Rx}^\circ(T_R) + \int_{T_R}^T \Delta C_p dT \right] F_{A0} \frac{dX}{dV} = 0 \end{aligned} \quad (8-55)$$

Recalling that $-r_A = F_{A0}(dX/dV)$, and substituting Equation (8-44) for $(d\dot{Q}/dV)$, we can rearrange Equation (8-55) to obtain

$$\frac{dT}{dV} = \frac{Ua(T_a - T) + (-r_A)[- \Delta H_{Rx}(T)]}{F_{A0}(\sum \Theta_i C_{pi} + X \Delta C_p)} \quad (8-56)$$

Energy balance on PFR with heat transfer

Energy balance

The differential equation describing the change of temperature with volume (i.e., distance) down the reactor,

$$\frac{dT}{dV} = g(X, T)$$

Numerical integration of two coupled differential equations is required

must be coupled with the mole balance,

$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}} = f(X, T)$$

Mole balance

and solved simultaneously. A variety of numerical integration schemes can be used to solve these two equations simultaneously.

Energy Balance in Measures Other Than Conversion. If we work in terms other than conversion, we derive an equation similar to Equation (8-56) by first differentiating Equation (8-10),

$$\dot{Q} - \dot{W}_s + \sum_{i=1}^n F_{i0} H_{i0} - \sum_{i=1}^n F_i H_i = 0 \quad (8-10)$$

with respect to the volume, V :

$$\frac{d\dot{Q}}{dV} - \frac{d\dot{W}_s}{dV} + 0 - \sum \frac{dF_i}{dV} H_i - \sum F_i \frac{dH_i}{dV} = 0 \quad (8-57)$$

From a mole balance on species i , we have

$$\frac{dF_i}{dV} = r_i = v_i(-r_A) \quad (8-58)$$

and from (8-44),

$$\frac{d\dot{Q}}{dV} = Ua(T_a - T)$$

Differentiating Equation (8-19) with respect to volume, V :

$$\frac{dH_i}{dV} = C_{pi} \frac{dT}{dV} \quad (8-59)$$

Neglecting the work term and substituting Equation (8-58), (8-59) and (8-44) into Equation (8-57), we obtain

$$Ua(T_a - T) - \sum v_i H_i(-r_A) - \sum F_i C_{pi} \frac{dT}{dV} = 0$$

Rearranging, we have

PFR/PBR

$$\frac{dT}{dV} = \frac{Ua(T_a - T) + (-\Delta H_{Rx})(-r_A)}{\sum F_i C_{pi}} \quad (8-60)$$

This equation is coupled with the mole balances on each species [Equation (8-58)]. Next we express r_A as a function of either the concentrations for liquid systems or molar flow rates for gas systems as described in Section 3.4.

For a CSTR the energy balance can be written as

$$UA(T_a - T) - \sum F_{i0} C_{pi}(T - T_0) + (-\Delta H_{Rx})(-r_A V) = 0 \quad (8-61)$$

Rearranging gives

CSTR

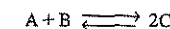
$$T = \frac{UAT_a + \sum F_{i0} C_{pi} T_0 + (-\Delta H_{Rx})(-r_A V)}{UA + \sum F_{i0} C_{pi}} \quad (8-62)$$

Table 8-3 gives the algorithm for the design of PFRs and PBRs with heat exchange for case A: conversion as the reaction variable and case B: molar flow rates as the reaction variable. The procedure in case B must be used when multiple reactions are present.

Having considered the exothermic liquid-phase reaction with constant heat capacities, we now consider an endothermic gas-phase reaction with variable heat capacities.

TABLE 8-3. PFR/PBR ALGORITHM FOR HEAT EFFECTS

A. Conversion as the reaction variable



1. Mole balance:

$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}} \quad (T8-3.1)$$

2. Rate law:

$$-r_A = k_A \left(C_A C_B - \frac{C_C^2}{K_C} \right) \quad (T8-3.2)$$

$$k = k_1(T_1) \exp \left[\frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T} \right) \right] \quad (T8-3.3)$$

for $\Delta \hat{C}_p \approx 0$.

$$K_C = K_{C2}(T_2) \exp \left[\frac{\Delta H_{Rx}^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T} \right) \right] \quad (T8-3.4)$$

3. Stoichiometry (gas phase, no ΔP):

$$C_A = C_{A0}(1 - X) \frac{T_0}{T} \quad (T8-3.5)$$

$$C_B = C_{A0}(\Theta_B - X) \frac{T_0}{T} \quad (T8-3.6)$$

$$C_C = 2C_{A0}X \frac{T_0}{T} \quad (T8-3.7)$$

4. Energy balance:

$$\frac{dT}{dV} = \frac{Ua(T_a - T) + (-r_A)(-\Delta H_{Rx})}{F_{A0}[C_{pA} + \Theta_B C_{pB} + X \Delta C_p]} \quad (T8-3.8)$$

B. Molar flow rates as the reaction variable

1. Mole balances:

$$\frac{dF_A}{dV} = r_A \quad (T8-3.9)$$

$$\frac{dF_B}{dV} = r_B \quad (T8-3.10)$$

$$\frac{dF_C}{dV} = r_C \quad (T8-3.11)$$

2. Rate law:

$$-r_A = k_A \left(C_A C_B - \frac{C_C^2}{K_C} \right) \quad (T8-3.2)$$

$$k = k_1(T_1) \exp \left[\frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T} \right) \right] \quad (T8-3.6)$$

for $\Delta \hat{C}_p \approx 0$.

$$K_C = K_{C2}(T_2) \exp \left[\frac{\Delta H_{Rx}^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T} \right) \right] \quad (T8-3.7)$$

These forms of the energy balance will be applied to multiple reactions

TABLE 8-3. (CONTINUED) PFR/PBR ALGORITHM FOR HEAT EFFECTS

3. Stoichiometry (gas phase, no ΔP):

$$r_B = r_A \quad (\text{T8-3.12})$$

$$r_C = 2r_A \quad (\text{T8-3.13})$$

$$C_A = C_{T0} \frac{F_A}{F_T} \frac{T_0}{T} \quad (\text{T8-3.14})$$

$$C_B = C_{T0} \frac{F_B}{F_T} \frac{T_0}{T} \quad (\text{T8-3.15})$$

$$C_C = C_{T0} \frac{F_C}{F_T} \frac{T_0}{T} \quad (\text{T8-3.16})$$

4. Energy balance:

$$\frac{dT}{dV} = \frac{Ua(T_a - T) + (-r_A)(-\Delta H_{Rx})}{F_A C_{pA} + F_B C_{pB} + F_C C_{pC}} \quad (\text{T8-3.17})$$

Enter parameter values:

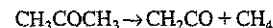
$$k_1, E, R, C_{T0}, T_a, T_0, T_1, T_2, K_{C2}, \Theta_B, \Delta H_{Rx}^\circ, C_{pA}, C_{pB}, C_{pC}, Ua$$

Enter initial values: $F_{A0}, F_{B0}, F_{C0}, F_{D0}, T_0$ and final values: $V_f =$ _____

Use ODE solver.

Example 8-7 Production of Acetic Anhydride

Jeffreys,⁸ in a treatment of the design of an acetic anhydride manufacturing facility, states that one of the key steps is the vapor-phase cracking of acetone to ketene and methane:



He states further that this reaction is first-order with respect to acetone and that the specific reaction rate can be expressed by

$$\ln k = 34.34 - \frac{34,222}{T} \quad (\text{E8-7.1})$$

where k is in reciprocal seconds and T is in kelvin. In this design it is desired to feed 8000 kg of acetone per hour to a tubular reactor. The reactor consists of a bank of 1000 1-inch schedule 40 tubes. We will consider two cases:

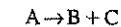
1. The reactor is operated *adiabatically*.
2. The reactor is surrounded by a *heat exchanger* where the heat-transfer coefficient is $110 \text{ J/m}^2 \cdot \text{s} \cdot \text{K}$, and the ambient temperature is 1150 K .

The inlet temperature and pressure are the same for both cases at 1035 K and 162 kPa (1.6 atm), respectively. Plot the conversion and temperature along the length of the reactor.

⁸ G. V. Jeffreys, *A Problem in Chemical Engineering Design: The Manufacture of Acetic Anhydride*, 2nd ed. (London: Institution of Chemical Engineers, 1964).

Solution

Let $A = \text{CH}_3\text{COCH}_3$, $B = \text{CH}_2\text{CO}$, and $C = \text{CH}_4$. Rewriting the reaction symbolically gives us



1. Mole balance:

$$\frac{dX}{dV} = -r_A/F_{A0} \quad (\text{E8-7.2})$$

2. Rate law:

$$-r_A = kC_A \quad (\text{E8-7.3})$$

3. Stoichiometry (gas-phase reaction with no pressure drop):

$$C_A = \frac{C_{A0}(1-X)T_0}{(1+\epsilon X)T} \quad (\text{E8-7.4})$$

$$\epsilon = y_{A0}\delta = 1(1+1-1) = 1$$

4. Combining yields

$$-r_A = \frac{kC_{A0}(1-X)T_0}{1+X} \frac{T_0}{T} \quad (\text{E8-7.5})$$

$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}} = \frac{k}{v_0} \left(\frac{1-X}{1+X} \right) \frac{T_0}{T} \quad (\text{E8-7.6})$$

To solve the differential equation above, it is first necessary to use the energy balance to determine T as a function of X .

5. Energy balance:

CASE I. ADIABATIC OPERATION

For no work done on the system, $\dot{W}_s = 0$, and adiabatic operation, $\dot{Q} = 0$ (i.e., $U = 0$), Equation (8-56) becomes

$$\frac{dT}{dV} = \frac{(-r_A) \left\{ -\left[\Delta H_{Rx}^\circ(T_R) + \int_{T_R}^T (\Delta\alpha + \Delta\beta T + \Delta\gamma T^2) dT \right] \right\}}{F_{A0} (\sum \Theta_i C_{pi} + X \Delta C_p)} \quad (\text{E8-7.7})$$

where in general

$$\Delta\alpha = \frac{d}{a} \alpha_D + \frac{c}{a} \alpha_C - \frac{b}{a} \alpha_B - \alpha_A$$

For acetone decomposition

$$\Delta\alpha = \alpha_B + \alpha_C - \alpha_A$$

Equivalent expressions exist for $\Delta\beta$ and $\Delta\gamma$.

Because only A enters,

$$\sum \Theta_i C_{pi} = C_{pA}$$

and Equation (E8-7.7) becomes

$$\frac{dT}{dV} = \frac{(-r_A) \left\{ -\left[\Delta H_{Rx}^\circ(T_R) + \int_{T_R}^T (\Delta\alpha + \Delta\beta T + \Delta\gamma T^2) dT \right] \right\}}{F_{A0}(C_{pA} + X \Delta C_p)}$$

Integrating gives

$$\frac{dT}{dV} = \frac{(-r_A) \left\{ -\left[\Delta H_{Rx}^\circ + \Delta\alpha(T - T_R) + \frac{\Delta\beta}{2}(T^2 - T_R^2) + \frac{\Delta\gamma}{3}(T^3 - T_R^3) \right] \right\}}{F_{A0}(\alpha_A + \beta_A T + \gamma_A T^2 + X \Delta C_p)} \quad (\text{E8-7.8})$$

6. Calculation of mole balance parameters:

$$F_{A0} = \frac{8000 \text{ kg/h}}{58 \text{ g/mol}} = 137.9 \text{ kmol/h} = 38.3 \text{ mol/s}$$

$$C_{A0} = \frac{P_{A0}}{RT} = \frac{162 \text{ kPa}}{8.31 \frac{\text{kJ}}{\text{kmol} \cdot \text{K}} (1035 \text{ K})} = 0.0188 \frac{\text{kmol}}{\text{m}^3} = 18.8 \text{ mol/m}^3$$

$$v_0 = \frac{F_{A0}}{C_{A0}} = 2.037 \text{ m}^3/\text{s}$$

7. Calculation of energy balance parameters:

a. $\Delta H_{Rx}^\circ(T_R)$: At 298 K, the standard heats of formation are

$$H_{Rx}^\circ(T_R)_{\text{acetone}} = -216.67 \text{ kJ/mol}$$

$$H_{Rx}^\circ(T_R)_{\text{ketene}} = -61.09 \text{ kJ/mol}$$

$$H_{Rx}^\circ(T_R)_{\text{methane}} = -74.81 \text{ kJ/mol}$$

$$\Delta H_{Rx}^\circ(T_R) = (-61.09) + (-74.81) - (-216.67) = 80.77 \text{ kJ/mol}$$

b. ΔC_p : The heat capacities are:

$$\text{CH}_3\text{COCH}_3: C_{pA} = 26.63 + 0.183T - 45.86 \times 10^{-6} T^2 \text{ J/mol} \cdot \text{K}$$

$$\text{CH}_2\text{CO}: C_{pB} = 20.04 + 0.0945T - 30.95 \times 10^{-6} T^2 \text{ J/mol} \cdot \text{K}$$

$$\text{CH}_4: C_{pC} = 13.39 + 0.077T - 18.71 \times 10^{-6} T^2 \text{ J/mol} \cdot \text{K}$$

$$\Delta\alpha = \alpha_C + \alpha_B - \alpha_A = 13.39 + 20.04 - 26.63 = 6.8 \text{ J/mol} \cdot \text{K}$$

$$\Delta\beta = \beta_C + \beta_B - \beta_A = 0.077 + 0.0945 - 0.183 = -0.0115 \text{ J/mol} \cdot \text{K}^2$$

$$\Delta\gamma = \gamma_C + \gamma_B - \gamma_A = (-18.71 \times 10^{-6}) + (-30.95 \times 10^{-6}) - (-45.86 \times 10^{-6}) = -3.8 \times 10^{-6} \text{ J/mol} \cdot \text{K}^3$$

Adiabatic PFR
with variable heat
capacities

Adiabatic PFR
with variable heat
capacities

$$\frac{\Delta\beta}{2} = -5.75 \times 10^{-3} \quad \frac{\Delta\gamma}{3} = -1.27 \times 10^{-6}$$

See Table E8-7.1 for a summary of the calculations and Table E8-7.2 and Figure E8-7.1 for the POLYMATH program and its graphical output.

TABLE E8-7.1. SUMMARY

$\frac{dX}{dV} = \frac{-r_A}{F_{A0}}$	(E8-7.2)
$-r_A = -\frac{kC_{A0}(1-X)}{(1+X)} \frac{T_0}{T}$	(E8-7.5)
$\frac{dT}{dV} = \frac{(-r_A) \left\{ -\left[\Delta H_{Rx}^\circ(T_R) + \Delta\alpha(T - T_R) + \frac{\Delta\beta}{2}(T^2 - T_R^2) + \frac{\Delta\gamma}{3}(T^3 - T_R^3) \right] \right\}}{F_{A0}(\alpha_A + \beta_A T + \gamma_A T^2 + X \Delta C_p)}$	(E8-7.8)
$\Delta C_p = 6.8 - 11.5 \times 10^{-3} T - 3.81 \times 10^{-6} T^2$	
$\Delta H_{Rx}^\circ(T_R) = 80.770$	
$\alpha_A = 26.63$	$\Delta\alpha = 6.8$
$\beta_A = 0.183$	$\frac{\Delta\beta}{2} = -5.75 \times 10^{-3}$
$\gamma_A = -45.86 \times 10^{-6}$	$\frac{\Delta\gamma}{3} = -1.27 \times 10^{-6}$
$C_{A0} = 18.8$	
$F_{A0} = 38.3$	
$k = 8.2 \times 10^{14} \exp\left(\frac{-34,222}{T}\right)$	(E8-7.12)

TABLE E8-7.2. POLYMATH PROGRAM

Equations:	Initial Values:
$d(T)/d(V) = -r_A \times (-\Delta H) / (F_{A0} \times (C_{pA} + X \Delta C_p))$	1035
$d(X)/d(V) = -r_A / F_{A0}$	0
$k = 8.2 \times 10^{14} \exp(-34222/T)$	
$F_{A0} = 38.3$	
$C_{pA} = 26.63 + 0.183T - 45.86 \times 10^{-6} T^2$	
$\Delta C_p = 6.8 - 11.5 \times 10^{-3} T - 3.81 \times 10^{-6} T^2$	
$C_{A0} = 18.8$	
$T_0 = 1035$	
$T_R = 298$	
$\Delta H = 80770 + 6.8 \times (T - T_R) - 5.75 \times 10^{-3} (T^2 - T_R^2) - 1.27 \times 10^{-6} (T^3 - T_R^3)$	
$r_A = -k C_{A0} (1-X) / (1+X) \times T_0 / T$	
$U_0 = 0, \quad U_f = 5$	

Adiabatic
endothermic
reaction in a PFR

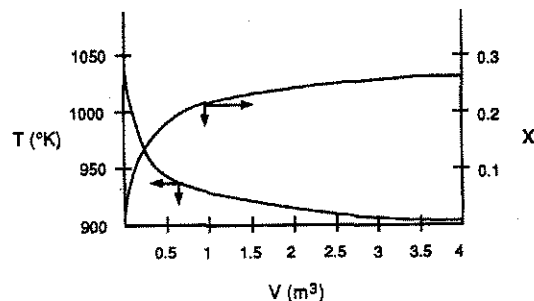


Figure E8-7.1

Note that for this adiabatic endothermic reaction, the reaction virtually *dies out* after 2.5 m³, owing to the large drop in temperature, and very little conversion is achieved beyond this point. One way to increase the conversion would be to add a diluent such as N₂, which could supply the sensible heat for this endothermic reaction. However, if too much diluent is added, the concentration and rate will be quite low. On the other hand, if too little diluent is added, the temperature will drop and virtually extinguish the reaction. How much diluent to add is left as an exercise (see Problem P8-2).

A bank of 1000 1-in. schedule 40 tubes 2.28 m in length corresponds to 1.27 m³ and gives 20% conversion. Ketene is unstable and tends to explode, which is a good reason to keep the conversion low. However, the pipe material and schedule size should be checked to learn if they are suitable for these temperatures and pressures.

CASE II. OPERATION OF A PFR WITH HEAT EXCHANGE

See Figure E8-7.2.

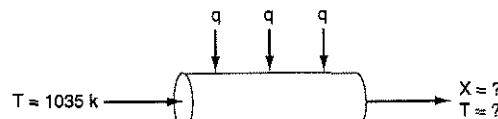


Figure E8-7.2 PFR with heat exchange.

1. The mole balance:

$$(1) \quad \frac{dX}{dV} = \frac{-r_A}{F_{A0}} \quad (\text{E8-7.2})$$

Using (2) the rate law (E8-7.3) and (3) stoichiometry (E8-7.4) for the adiabatic case discussed previously, we (4) combine to obtain the reaction rate as

$$(4) \quad -r_A = kC_{A0} \left(\frac{1-X}{1+X} \right) \frac{T_0}{T} \quad (\text{E8-7.5})$$

5. Energy balance. Equation (8-56):

$$\frac{dT}{dV} = \frac{Ua(T_a - T) + (-r_A)[- \Delta H_{Rk}(T)]}{F_{A0}(\sum \Theta_i C_{pi} + X \Delta C_p)} \quad (\text{E8-7.9})$$

For the acetone reaction system,

$$\frac{dT}{dV} = \frac{Ua(T_a - T) + (r_A)[\Delta H_{Rk}(T)]}{F_{A0}(C_{pA} + X \Delta C_p)} \quad (\text{E8-7.10})$$

6. Parameter evaluation:

a. *Mole balance.* On a per tube basis, $v_0 = 0.002 \text{ m}^3/\text{s}$. The concentration of acetone is 18.8 mol/m^3 , so the entering molar flow rate is

$$F_{A0} = C_{A0}v_0 = \left(18.8 \frac{\text{mol}}{\text{m}^3} \right) \left(2 \times 10^{-3} \frac{\text{m}^3}{\text{s}} \right) = 0.0376 \frac{\text{mol}}{\text{s}}$$

The value of k at 1035 K is 3.58 s^{-1} ; consequently, we have

$$k(T) = 3.58 \exp \left[34,222 \left(\frac{1}{1035} - \frac{1}{T} \right) \right] \quad (\text{E8-7.11})$$

b. *Energy balance.* From the adiabatic case above we already have ΔC_p , C_{pA} , α_A , β_A , γ_A , $\Delta\alpha$, $\Delta\beta$, and $\Delta\gamma$. The heat-transfer area per unit volume of pipe is

$$a = \frac{\pi DL}{(\pi D^2/4)L} = \frac{4}{D} = \frac{4}{0.0266 \text{ m}} = 150 \text{ m}^{-1}$$

$$U = 110 \text{ J/m}^2 \cdot \text{s} \cdot \text{K}$$

Combining the overall heat-transfer coefficient with the area yields

$$Ua = 16,500 \text{ J/m}^3 \cdot \text{s} \cdot \text{K}$$

We now use Equations (E8-7.1) through (E8-7.6), and Equations (E8-7.10) and (E8-7.11) along with the POLYMATH program (Table E8-7.4), to determine the conversion and temperature profiles shown in Figure E8-7.3.

The corresponding variables in the POLYMATH program are

$$t1 = T, \quad dh = \Delta H_{Rk}(T), \quad dcp = \Delta C_p, \quad cpa = C_{pA}, \quad ua = Ua$$

TABLE E8-7.4. POLYMATH PROGRAM FOR PFR WITH HEAT EXCHANGE

Equations:	Initial Values:
$d(t)/d(v) = (ua \times (ta - t) + ra \times dh) / (fa0 \times (cpa + x \times dcp))$	1035
$d(x)/d(v) = -ra / fa0$	0
$fa0 = 0.0376$	
$ua = 16500$	
$ta = 1150$	
$cpa = 26.8 + 0.183 \times t - 0.000459 \times t^2$	
$dcp = 6.8 - 0.115 \times t - 0.0000381 \times t^2$	
$ca0 = 18.8$	
$t0 = 1035$	
$term = -0.0000127 \times (t \times t^3 - 298 \times t^3)$	
$dh = 80770 + 6.8 \times (t - 298) - 0.0575 \times (t^2 - 298 \times t^2) + term$	
$ra = -ca0 \times 3.58 \times \exp(34222 \times (1/t0 - 1/t)) \times (1-x) \times (t0/t) / (1+x)$	
$v0 = 0, \quad v_f = 0.001$	

PFR with heat exchange

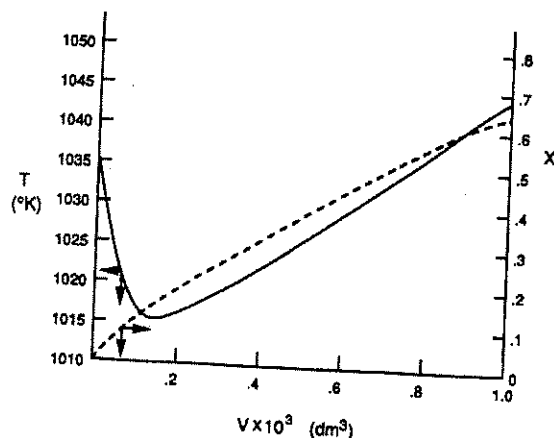


Figure E8-7.3 Temperature and conversion profiles in PFR.

One notes the reactor temperature goes through a minimum along the length of the reactor. At the front of the reactor the reaction takes place very rapidly, drawing energy from the sensible heat of the gas causing the gas temperature to drop because the heat exchanger cannot supply energy at the equal or greater rate. This drop in temperature, coupled with the consumption of reactants, slows the reaction rate as we move down the reactor. Because of this slower reaction rate, the heat exchanger supplies energy at a rate greater than reaction draws energy from the gases and as a result the temperature increases.

8.4 Equilibrium Conversion

For reversible reactions, the equilibrium conversion, X_e , is usually calculated first

The highest conversion that can be achieved in reversible reactions is the equilibrium conversion. For endothermic reactions, the equilibrium conversion increases with increasing temperature up to a maximum of 1.0. For exothermic reactions the equilibrium conversion decreases with increasing temperature.

8.4.1 Adiabatic Temperature and Equilibrium Conversion

Exothermic Reactions. Figures 8-6 and 8-7 show typical plots of equilibrium conversion as a function of temperature for an exothermic reaction. To determine the maximum conversion that can be achieved in an exothermic reaction carried out adiabatically, we find the intersection of the equilibrium conversion as a function of temperature with temperature-conversion relationships from the energy balance (Figure 8-7). For $T_{i0} = T_0$,

$$X_{EB} = \frac{\sum \Theta_i \tilde{C}_{pi}(T - T_0)}{-\Delta H_{Rx}(T)} \quad (E8-4.6)$$

For exothermic reactions, equilibrium conversion decreases with increasing temperature

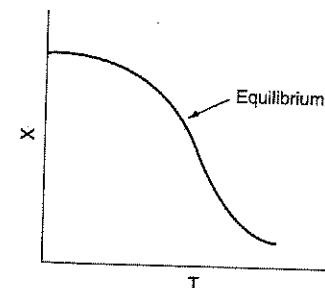


Figure 8-6 Variation of equilibrium constant and conversion with temperature for an exothermic reaction.

Adiabatic equilibrium conversion for exothermic reactions

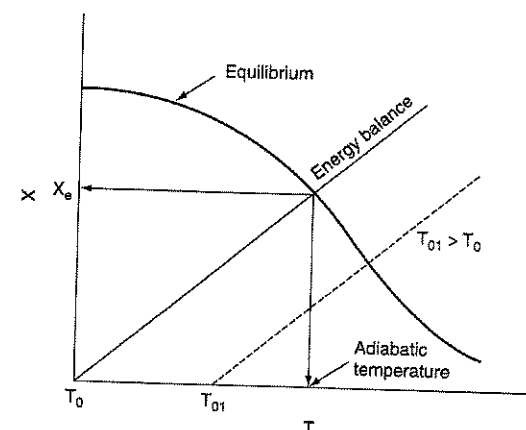
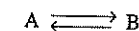


Figure 8-7 Graphical solution of equilibrium and energy balance equations to obtain adiabatic temperature and equilibrium conversion.

If the entering temperature is increased from T_0 to T_{01} , the energy balance line will be shifted to the right and will be parallel to the original line, as shown by the dashed line. Note that as the inlet temperature increases, the adiabatic equilibrium conversion decreases.

Example 8-8 Calculating the Adiabatic Equilibrium Temperature

For the elementary solid-catalyzed liquid-phase reaction



make a plot of equilibrium conversion as a function of temperature. Determine the adiabatic equilibrium temperature and conversion when pure A is fed to the reactor at a temperature of 300 K.

Additional information:

$$\begin{aligned} H_A^\circ(298 \text{ K}) &= -40,000 \text{ cal/mol} & H_B^\circ(298 \text{ K}) &= -60,000 \text{ cal/mol} \\ C_{pA} &= 50 \text{ cal/mol} \cdot \text{K} & C_{pB} &= 50 \text{ cal/mol} \cdot \text{K} \\ K_e &= 100,000 \text{ at } 298 \text{ K} \end{aligned}$$

Solution

1. Rate law:

$$-r_A = k \left(C_A - \frac{C_B}{K_e} \right) \quad (\text{E8-8.1})$$

2. Equilibrium, $-r_A = 0$; so

$$C_{Ae} = \frac{C_{Be}}{K_e}$$

3. Stoichiometry ($v = v_0$) yields

$$C_{A0}(1 - X_e) = \frac{C_{A0}X_e}{K_e}$$

Solving for X_e gives

$$X_e = \frac{K_e(T)}{1 + K_e(T)} \quad (\text{E8-8.2})$$

4. Equilibrium constant. Calculate ΔC_p , then $K_e(T)$:

$$\Delta C_p = C_{pB} - C_{pA} = 50 - 50 = 0 \text{ cal/mol} \cdot \text{K}$$

For $\Delta C_p = 0$, the equilibrium constant varies with temperature according to the relation

$$K_e(T) = K_e(T_1) \exp \left[\frac{\Delta H_{Rx}^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T} \right) \right] \quad (\text{E8-8.3})$$

$$\Delta H_{Rx}^\circ = H_B^\circ - H_A^\circ = -20,000 \text{ cal/mol}$$

$$K_e(T) = 100,000 \exp \left[\frac{-20,000}{1.987} \left(\frac{1}{298} - \frac{1}{T} \right) \right]$$

$$K_e = 100,000 \exp \left[-33.78 \left(\frac{T - 298}{T} \right) \right] \quad (\text{E8-8.4})$$

Substituting Equation (E8-8.4) into (E8-8.2) we can calculate equilibrium conversion as a function of temperature:

$$X_e = \frac{100,000 \exp [-33.78(T - 298)/T]}{1 + 100,000 \exp [-33.78(T - 298)/T]} \quad (\text{E8-8.5})$$

Conversion
calculated from
equilibrium
relationship

The calculations are shown in Table E8-8.1.

TABLE E8-8.1. EQUILIBRIUM CONVERSION
AS A FUNCTION OF TEMPERATURE

T	K_e	X_e
298	100,000.00	1.00
350	661.60	1.00
400	18.17	0.95
425	4.14	0.80
450	1.11	0.53
475	0.34	0.25
500	0.12	0.11

For a reaction carried out adiabatically, the energy balance reduces to

$$X_{EB} = \frac{\sum \Theta_i \tilde{C}_{pi}(T - T_0)}{-\Delta H_{Rx}} = \frac{C_{pA}(T - T_0)}{-\Delta H_{Rx}} \quad (\text{E8-8.6})$$

$$X_{EB} = \frac{50(T - 300)}{20,000} = 2.5 \times 10^{-3}(T - 300) \quad (\text{E8-8.7})$$

Conversion
calculated from
energy balance

Data from Table E8-8.1 and the following data are plotted in Figure E8-8.1.

T (K)	300	400	500	600
X_{EB}	0	0.25	0.50	0.75

$$X_e = 0.41 \quad T_e = 465 \text{ K}$$

For a feed temperature of 300 K, the adiabatic equilibrium temperature is 465 K and the corresponding adiabatic equilibrium conversion is 0.41.

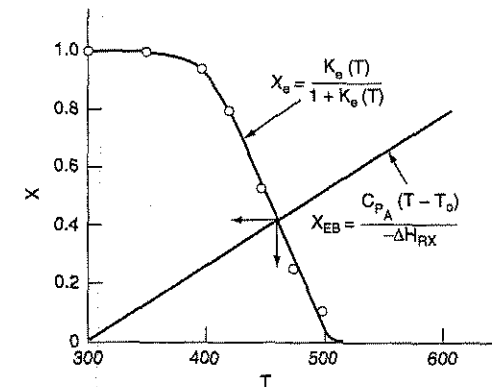
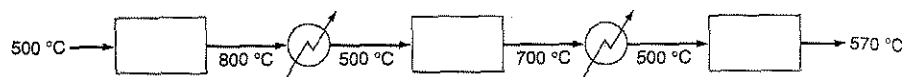


Figure E8-8.1 Finding the adiabatic equilibrium temperature (T_e) and conversion (X_e).

Higher conversions than those shown in Figure E8-8.1 can be achieved for adiabatic operations by connecting reactors in series with interstage cooling:



The conversion-temperature plot for this scheme is shown in Figure 8-8.

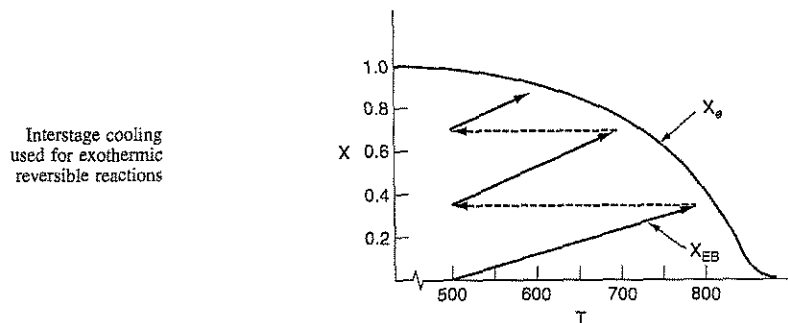
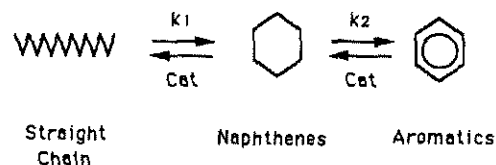


Figure 8-8 Increasing conversion by interstage cooling.

Endothermic Reactions. Another example of the need for interstage heat transfer in a series of reactors can be found when upgrading the octane number of gasoline. The more compact the hydrocarbon molecule for a given number of carbon atoms, the higher the octane rating. Consequently, it is desirable to convert straight-chain hydrocarbons to branched isomers, naphthenes, and aromatics. The reaction sequence is



The first reaction step (k_1) is slow compared to the second step, and each step is highly endothermic. The allowable temperature range for which this reaction can be carried out is quite narrow: Above 530°C undesirable side reactions occur and below 430°C the reaction virtually does not take place. A typical feed stock might consist of 75% straight chains, 15% naphthas, and 10% aromatics.

One arrangement currently used to carry out these reactions is shown in Figure 8-9. Note that the reactors are not all the same size. Typical sizes are on the order of 10 to 20 m high and 2 to 5 m in diameter. A typical feed rate of

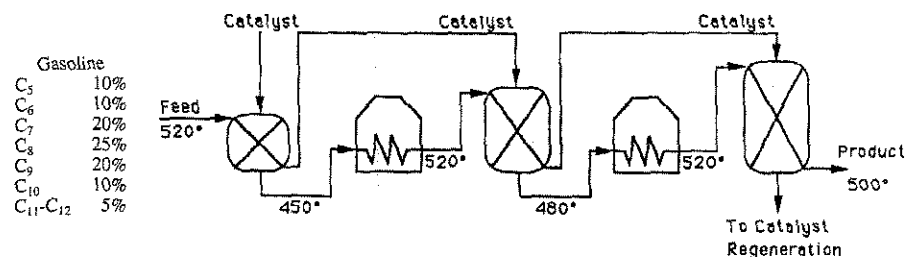


Figure 8-9 Interstage heating for gasoline production in moving-bed reactors.

Typical values for gasoline production

gasoline is approximately 200 m³/h at 2 atm. Hydrogen is usually separated from the product stream and recycled.

Because the reaction is endothermic, equilibrium conversion increases with increasing temperature. A typical equilibrium curve and temperature-conversion trajectory for the reactor sequence are shown in Figure 8-10.

Interstage heating

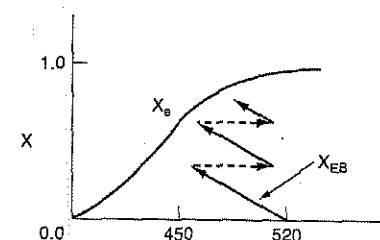


Figure 8-10 Temperature-conversion trajectory for interstage heating of an endothermic reaction corresponding to Figure 8-9.

Example 8-9 Interstage Cooling

What conversion could be achieved in Example 8-8 if two interstage coolers were available that had the capacity to cool the exit stream to 350°K? Also determine the heat duty of each exchanger for a molar feed rate of A of 40 mol/s. Assume that 95% of equilibrium conversion is achieved in each reactor. The feed temperature to the first reactor is 300 K.

We saw in Example 8-8 that for an entering temperature of 300 K the adiabatic equilibrium conversion was 0.41. For 95% of equilibrium conversion, the conversion exiting the first reactor is 0.4. The exit temperature is found from a rearrangement of Equation (E8-8.7):

$$T = 300 + 400X = 300 + (400)(0.4)$$

$$T_1 = 460 \text{ K}$$

We now cool the gas stream exiting the reactor at 460 K down to 350 K in a heat exchanger (Figure E8-9.1).

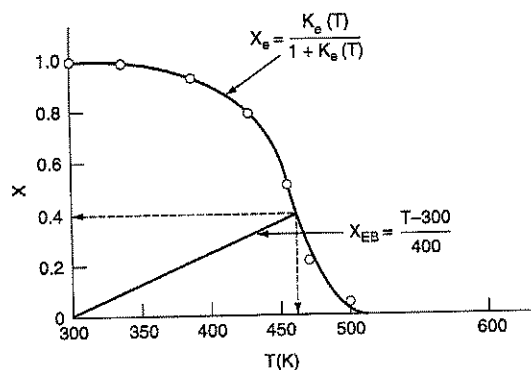


Figure E8-9.1 Determining exit conversion and temperature in the first stage.

There is no work done on the reaction gas mixture in the exchanger and the reaction does not take place in the exchanger. Under these conditions ($F_{i,in} = F_{i,out}$) the energy balance given by Equation (8-10),

$$\dot{Q} - \dot{W}_s + \sum F_{i0} H_i - \sum F_i H_i = 0 \quad (8-10)$$

becomes

$$\dot{Q} = \sum F_i H_i - \sum F_{i0} H_{i0} = \sum F_{i0} (H_i - H_{i0}) \quad (E8-9.1)$$

$$= \sum F_i \hat{C}_{p_i} (T_2 - T_1) = (F_A \hat{C}_{p_A} + F_B \hat{C}_{p_B}) (T_2 - T_1) \quad (E8-9.2)$$

But $\hat{C}_{p_A} = \hat{C}_{p_B}$,

$$\dot{Q} = (F_A + F_B) (\hat{C}_{p_A}) (T_2 - T_1) \quad (E8-9.3)$$

Also, $F_{A0} = F_A + F_B$,

$$\begin{aligned} \dot{Q} &= F_{A0} \hat{C}_{p_A} (T_2 - T_1) \\ &= \frac{40 \text{ mol}}{\text{s}} \cdot \frac{50 \text{ mol}}{\text{mol} \cdot \text{K}} (350 - 460) \\ &= -220 \frac{\text{kcal}}{\text{s}} \end{aligned} \quad (E8-9.4)$$

We see that 220 kcal/s is removed from the reaction system mixture. The rate at which energy must be absorbed by the coolant stream in the exchanger is

$$\dot{Q} = \dot{m}_C \hat{C}_{p_C} (T_{\text{out}} - T_{\text{in}}) \quad (E8-9.5)$$

We consider the case where the coolant is available at 270 K but cannot be heated above 400 K and calculate the coolant flow rate necessary to remove 220 kcal/s from the reaction mixture. Rearranging Equation (E8-9.5) and noting that the coolant heat capacity is 18 cal/mol·K gives

Sizing the interstage heat exchanger and coolant flow rate

Bonding with Unit Operations

Sizing the heat exchanger

$$\begin{aligned} \dot{m}_C &= \frac{\dot{Q}}{\hat{C}_{p_C} (T_{\text{out}} - T_{\text{in}})} = \frac{220,000 \text{ cal/s}}{18 \frac{\text{cal}}{\text{mol} \cdot \text{K}} (400 - 270)} \\ &= 94 \text{ mol/s} = 1692 \text{ g/s} = 1.69 \text{ kg/s} \end{aligned} \quad (E8-9.6)$$

The necessary coolant flow rate is 1.69 kg/s.

Let's next determine the countercurrent heat exchanger area. The exchanger inlet and outlet temperatures are shown in Figure E8-9.2. The rate of heat transfer in a countercurrent heat exchanger is given by the equation⁹

$$\dot{Q} = UA \frac{[(T_{h2} - T_{c2}) - (T_{h1} - T_{c1})]}{\ln \left(\frac{T_{h2} - T_{c2}}{T_{h1} - T_{c1}} \right)} \quad (E8-9.7)$$

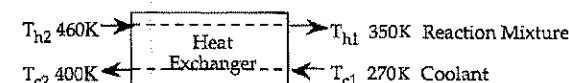


Figure E8-9.2 Countercurrent heat exchanger.

Rearranging Equation (E8-9.7) assuming a value of U of 1000 cal/s·m²·K, and then substituting the appropriate values gives

$$\begin{aligned} A &= \frac{\dot{Q} \ln \left(\frac{T_{h2} - T_{c2}}{T_{h1} - T_{c1}} \right)}{U [(T_{h2} - T_{c2}) - (T_{h1} - T_{c1})]} = \frac{220,000 \frac{\text{cal}}{\text{s}} \ln \left(\frac{460 - 400}{350 - 270} \right)}{1000 \frac{\text{cal}}{\text{s} \cdot \text{m}^2 \cdot \text{K}} [(460 - 400) - (350 - 270)] \text{ K}} \\ &= \frac{220 \ln(0.75)}{-20} \text{ m}^2 \\ &= 3.16 \text{ m}^2 \end{aligned}$$

The heat-exchanger surface area required to accomplish this rate of heat transfer is 3.16 m².

Now let's return to determine the conversion in the second reactor. The conditions entering the second reactor are $T = 350$ and $X = 0.4$. The energy balance starting from this point is shown in Figure E8-9.3. The corresponding adiabatic equilibrium conversion is 0.63. Ninety-five percent of the equilibrium conversion is 60% and the corresponding exit temperature is $T = 350 + (0.6 - 0.4)400 = 430$ K.

The heat-exchange duty to cool the reacting mixture from 430 K back to 350 K can be calculated from Equation (E8-9.4):

$$\begin{aligned} \dot{Q} &= F_{A0} \hat{C}_{p_A} (350 - 430) = \left(\frac{40 \text{ mol}}{\text{s}} \right) \left(\frac{50 \text{ cal}}{\text{mol} \cdot \text{K}} \right) (-80) \\ &= -160 \frac{\text{kcal}}{\text{s}} \end{aligned}$$

⁹ See page 271 of C. J. Geankoplis, *Transport Processes and Unit Operations* (Upper Saddle River, N.J.: Prentice Hall, 1993).

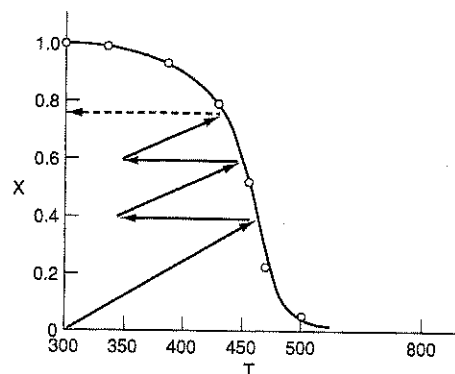


Figure E8-9.3 Three reactors in series with interstage cooling.

For the final reactor we begin at $T_0 = 350$ K and $X = 0.6$ and follow the line representing the equation for the energy balance along to the point of intersection with the equilibrium conversion, which is $X = 0.8$. Consequently, the final conversion achieved with three reactors and two interstage coolers is $(0.95)(0.8) = 0.76$.

8.4.2 Optimum Feed Temperature

We now consider an adiabatic reactor of fixed size or catalyst weight and investigate what happens as the feed temperature is varied. The reaction is reversible and exothermic. At one temperature extreme, using a very high feed temperature, the specific reaction rate will be large and the reaction will proceed rapidly, but the equilibrium conversion will be close to zero. Consequently, very little product will be formed. A plot of the equilibrium conversion and the conversion calculated from the adiabatic energy balance,

$$T = T_0 - \frac{\Delta H_{RX}^\circ}{\hat{C}_{PA} + \hat{C}_{PB}} X = T_0 + 400X$$

is shown in Figure 8-11. We see that for an entering temperature of 600 K the adiabatic equilibrium conversion is 0.15. The corresponding conversion profile down the length of the reactor is shown in Figure 8-12. We see that because of the high entering temperature the rate is very rapid and equilibrium is achieved very near the reactor entrance.

We notice that the conversion and temperature increase very rapidly over a short distance (i.e., a small amount of catalyst). This sharp increase is sometimes referred to as the point/temperature at which the reaction ignites. If the inlet temperature were lowered to 500 K, the corresponding equilibrium conversion is increased to 0.33; however, the reaction rate is slower at this lower temperature, so that this conversion is not achieved until close to the end of the

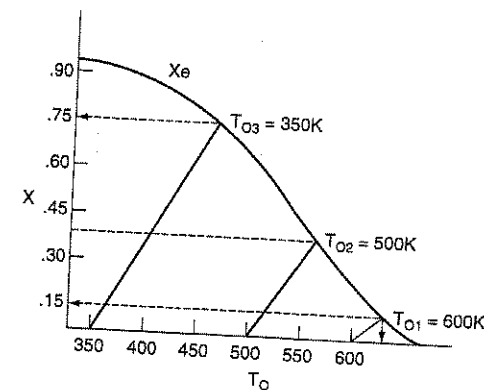


Figure 8-11 Equilibrium conversion for different feed temperatures.

Observe how the temperature profile changes as the entering temperature is decreased from 600 K

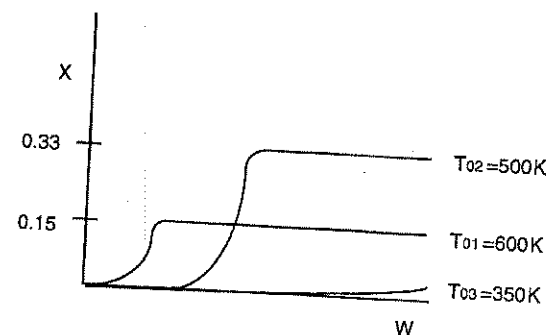


Figure 8-12 Conversion profiles for different feed temperatures.

reactor. If the entering temperature were lowered further to 350, the corresponding equilibrium conversion is 0.75, but the rate is so slow that a conversion of 0.05 is achieved for the catalyst weight in the reactor. At a very low feed temperature, the specific reaction rate will be so small that virtually all of the reactant will pass through the reactor without reacting. It is apparent that with conversions close to zero for both high and low feed temperatures there must be an optimum feed temperature that maximizes conversion. As the feed temperature is increased from a very low value, the specific reaction rate will increase, as will the conversion. The conversion will continue to increase with increasing feed temperature until the equilibrium conversion is approached in the reaction. Further increases in feed temperature will only decrease the conversion due to the decreasing equilibrium conversion. This optimum inlet temperature is shown in Figure 8-13.

Optimum inlet temperature

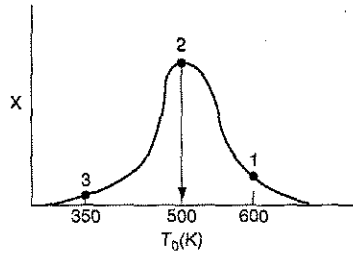
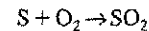


Figure 8-13 Finding the optimum feed temperature.

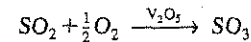
8.5 Nonadiabatic Reactor Operation: Oxidation of Sulfur Dioxide Example

8.5.1 Manufacture of Sulfuric Acid

In the manufacture of sulfuric acid from sulfur, the first step is the burning of sulfur in a furnace to form sulfur dioxide:



Following this step, the sulfur dioxide is converted to sulfur trioxide, using a catalyst:



A flowsheet of a typical sulfuric acid manufacturing plant is shown in Figure 8-14. It is the converter that we shall be treating in this section.

Although platinum catalysts once were used in the manufacture of sulfuric acid, the only catalysts presently in use employ supported vanadia.¹⁰ For our problem we shall use a catalyst studied by Eklund, whose work was echoed extensively by Donovan¹¹ in his description of the kinetics of SO_2 oxidation. The catalyst studied by Eklund was a Reymersholm V_2O_5 catalyst deposited on a pumice carrier. The cylindrical pellets had a diameter of 8 mm and a length of 8 mm, with a bulk density of 33.8 lb/ft³. Between 818 and 1029°F, the rate law for SO_2 oxidation over this particular catalyst was

$$-r'_{\text{SO}_2} = k \frac{P_{\text{SO}_2}}{P_{\text{SO}_3}} \left[P_{\text{O}_2} - \left(\frac{P_{\text{SO}_3}}{K_p P_{\text{SO}_2}} \right)^2 \right] \quad (8-63)$$

¹⁰G. M. Cameron, *Chem. Eng. Prog.*, 78(2), 71 (1982).

¹¹R. B. Eklund, Dissertation, Royal Institute of Technology, Stockholm, 1956, as quoted by J. R. Donovan, in *The Manufacture of Sulfuric Acid*, ACS Monograph Series 144, W. W. Duecker and J. R. West, eds. (New York: Reinhold, 1959), pp. 166–168.

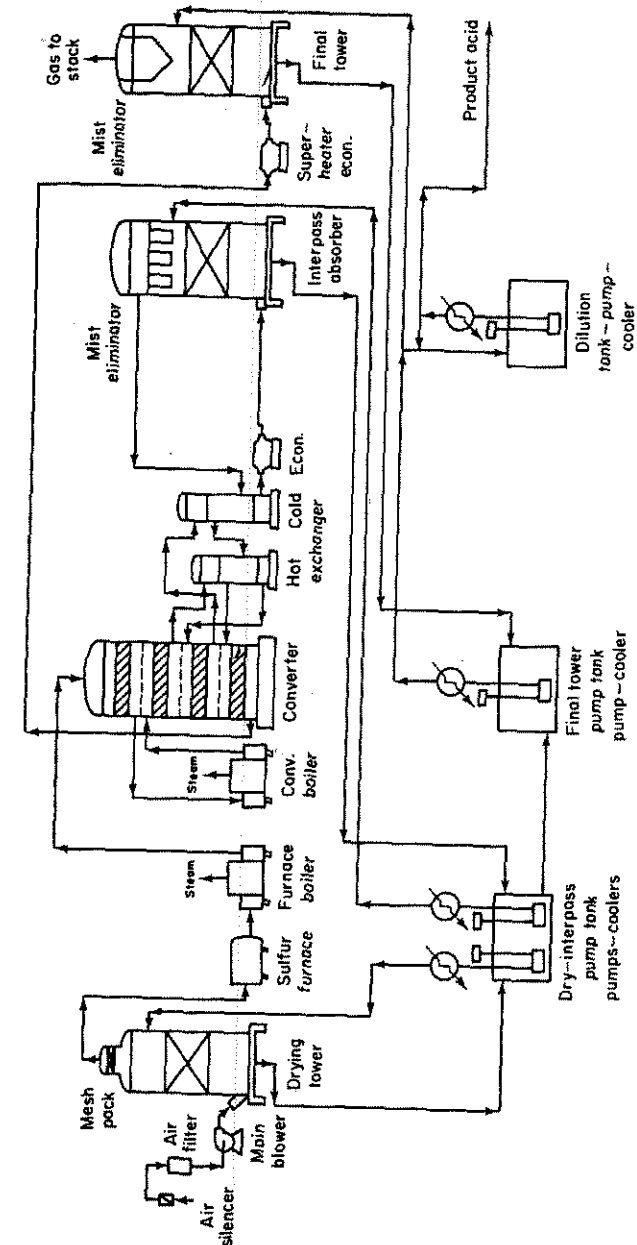


Figure 8-14 Flowsheet of a sulfuric acid manufacturing process. [Reprinted with permission of the AIChE and L. J. Friedman. Copyright © 1982 AIChE. All rights reserved.]

in which P_i was the partial pressure of species i . This equation can be used when the conversion is greater than 5%. At all conversions below 5%, the rate is essentially that for 5% conversion.

Sulfuric acid manufacturing processes use different types of reactors. Perhaps the most common type has the reactor divided into adiabatic sections with cooling between the sections (recall Figure 8-8). One such layout is shown in Figure 8-15. In the process in Figure 8-15, gas is brought out of the converter to cool it between stages, using the hot converter reaction mixture to preheat boiler feedwater, produce steam, superheat steam, and reheat the cold gas, all to increase the energy efficiency of the process. Another type has cooling tubes embedded in the reacting mixture. The one illustrated in Figure 8-16 uses incoming gas to cool the reacting mixture.

A typical sulfuric acid plant built in the 1970s produces 1000 to 2400 tons of acid/day.¹² Using the numbers of Kastens and Hutchinson,¹³ a 1000-ton/day sulfuric acid plant might have a feed to the SO_2 converter of 7900 lb mol/h,

An SO_2 flow rate of 0.241 mol/s over 132.158 lb of catalyst can produce 1000 tons of acid per day

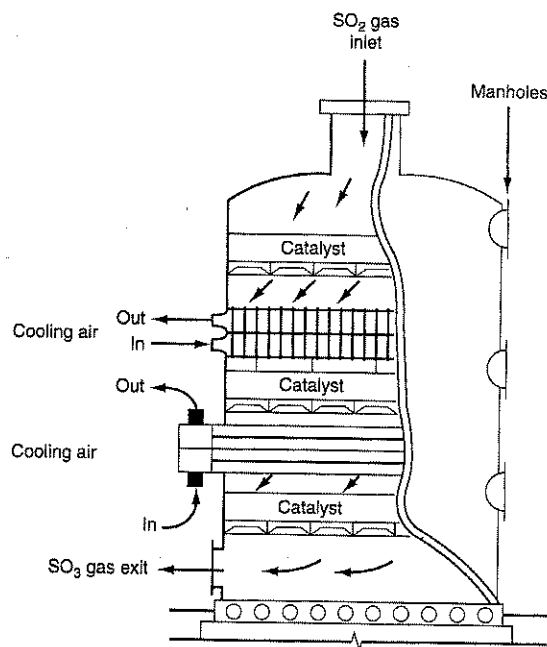


Figure 8-15 Sulfur dioxide converter with internal cooling between catalyst layers. [Reprinted with permission of Barnes & Noble Books.]

¹²L. F. Friedman, *Chem. Eng. Prog.*, 78(2), 51 (1982).

¹³M. L. Kastens and J. C. Hutchinson, *Ind. Eng. Chem.*, 40, 1340 (1948).

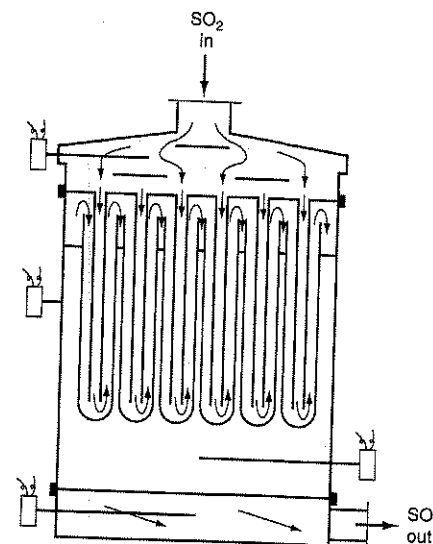


Figure 8-16 Sulfur dioxide converter with catalyst cooled by incoming reaction mixture. [Reprinted with permission of Barnes & Noble Books.]

consisting of 11% SO_2 , 10% O_2 , and 79% inerts (principally N_2). We shall use these values.

For preliminary design purposes, we shall calculate the conversions for two situations and compare the results. Only one of the situations will be presented in detail in this example. The other is given as a problem on the CD-ROM, but the answer will be used in the comparison.

1. The first situation concerns two stages of a typical commercial adiabatic reactor. The principles of calculating the conversion in an adiabatic reactor were covered earlier and illustrated in Section 8.3, so will not be presented here but as a problem at the end of the chapter.
2. The second case concerns a reactor with the catalyst in tubes, with the walls cooled by a constant-temperature boiling liquid. Calculations for this system are presented in detail below.

8.5.2 Catalyst Quantities

Harrer¹⁴ states that the volumetric flow rate in an adiabatic SO_2 converter, measured at normal temperature and pressure, customarily is about 75 to 100 $\text{ft}^3/\text{min} \cdot \text{ft}^2$ of converter area. He also states that the catalyst beds in the converter may be from 20 to 50 in. deep.

¹⁴T. S. Harrer, in *Kirk-Othmer Encyclopedia of Chemical Technology*, 2nd ed., Vol. 19 (New York: Wiley-Interscience, 1969), p. 470.

It is desirable to have a low mass velocity through the bed to minimize blower energy requirements, so the $75 \text{ ft}^3/\text{min} \cdot \text{ft}^2$ value will be used. Normal conversions in adiabatic converters are 70% in the first stage and an additional 18% in the second.¹⁵ Using Eklund's Reymersholm catalyst, solution of the adiabatic reactor problem at the end of the chapter shows that these conversions require 1550 ft^3 (23 in. deep) in the first stage and 2360 ft^3 (35 in. deep) in the second. As a result, in our cooled tubular reactor, we shall use a total catalyst volume of 3910 ft^3 .

8.5.3 Reactor Configuration

The catalyst is packed in tubes, and the tubes are put in heat exchangers where they will be cooled by a boiling liquid. The outside diameter of the tubes will be 3 in. Severe radial temperature gradients have been observed in SO_2 oxidation systems,¹⁶ although these systems had platinum catalysts and greatly different operating conditions than those being considered here. The 3-in. diameter is chosen as a compromise between minimizing temperature gradients and keeping the number of tubes low. For this service, 12-gauge thickness is specified, which means a thickness of 0.109 in. and an inside diameter of 2.782 in. A 20-ft length will be used, as a compromise between decreasing blower energy requirements (shorter tube length) and lowering capital costs (fewer tubes from a longer tube length). For 3910 ft^3 of catalyst, the number of tubes that will be required is

$$N_t = \frac{\text{volume of catalyst}}{\text{volume per tube}} = \frac{3910}{(20)(\pi)(2.782/12)^2/4} = 4631 \text{ tubes}$$

The total cross-sectional area of the tubes is

$$A_c = \frac{3910 \text{ ft}^3}{20 \text{ ft}} = 195.5 \text{ ft}^2$$

The overall heat-transfer coefficient between the reacting gaseous mixture and the boiling coolant is assumed to be $10 \text{ Btu}/\text{h} \cdot \text{ft}^2 \cdot ^\circ\text{F}$. This coefficient is toward the upper end of the range of heat-transfer coefficients for such situations as reported by Colburn and Bergelin.¹⁷

8.5.4 Operating Conditions

Sulfur dioxide converters operate at pressures only slightly higher than atmospheric. An absolute pressure of 2 atm will be used in our designs. The inlet

¹⁵J. R. Donovan and J. M. Salamone, in *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd ed., Vol. 22 (New York: Wiley-Interscience, 1978), p. 190.

¹⁶For example, R. W. Olson, R. W. Schuler, and J. M. Smith, *Chem Eng. Prog.*, 46, 614 (1950); and R. W. Schuler, V. P. Stallings, and J. M. Smith, *Chem. Eng. Prog. Symp. Ser.* 48(4), 19 (1952).

¹⁷Colburn and Bergelin, in *Chemical Engineers' Handbook*; 3rd ed. (New York: McGraw-Hill, 1950).

temperature to the reactor will be adjusted so as to give the maximum conversion. Two constraints are present here. The reaction rate over V_2O_5 catalyst is negligible below $\sim 750^\circ\text{F}$, and the reactor temperature should not exceed $\sim 1125^\circ\text{F}$ at any point.¹⁸ A series of inlet temperatures should be tested, and the one above 760°F giving the maximum conversion, yet having no reactor temperature exceeding 1120°F , should be used.

The cooling substance should operate at a high temperature so as to improve thermal efficiency by reuse of heat. The most suitable substance appears to be Dowtherm A, with a normal operating limit of $\sim 750^\circ\text{F}$ but which on occasion has been used as the coolant in this preliminary design.¹⁹

Example 8-10 Oxidation of SO_2

The feed to an SO_2 converter is 7900 lb mol/h and consists of 11% SO_2 , 10% O_2 , and 79% inerts (principally N_2). The converter consists of 4631 tubes packed with catalyst, each 20 ft long. The tubes are 3 in. o.d. and 2.782 in. i.d. The tubes will be cooled by a boiling liquid at 805°F , so the coolant temperature is constant over this value. The entering pressure is 2 atm.

For inlet temperatures of 740 and 940°F , plot the conversion, temperature, equilibrium conversion, and reaction rate profile down the reactor.

Additional information:

$$\begin{aligned} \phi &= 0.45 & U &= 10 \text{ Btu}/\text{h} \cdot \text{ft}^2 \cdot \text{R} \\ \rho_0 &= 0.054 \text{ lb}/\text{ft}^3 & A_c &= 0.0422 \text{ ft}^2 \\ P_0 &= 2 \text{ atm} & T_0 &= 1400^\circ\text{R} \text{ (also } T_0 = 1200 \text{ R)} \\ D_p &= 0.015 \text{ ft} & g_c &= 4.17 \times 10^8 \text{ lb}_m \cdot \text{ft}/\text{lb}_f \cdot \text{h}^2 \\ \mu &= 0.090 \text{ lb}/\text{ft} \cdot \text{h at } 1400 \text{ R} & \rho_b &= 33.8 \text{ lb}/\text{ft}^3 \text{ (bulk density)} \end{aligned}$$

Using recent JANAF²⁰ values of K_p at 700 and 900 K, the equilibrium constant at any temperature T is

$$K_p = \exp\left(\frac{42,311}{RT} - 11.24\right) \quad (K_p \text{ in atm}^{-1/2}, T \text{ in R}) \quad (\text{E8-10.1})$$

at 1600°R ,

$$K_p \approx 7.8 \text{ atm}^{-1/2}$$

¹⁸J. R. Donovan and J. M. Salamone, in *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd ed. (New York: Wiley, 1984).

¹⁹The vapor pressure of Dowtherm A at 805°F is very high, and this pressure would have to be maintained in the shell side of the reactor for boiling Dowtherm A to be used as a coolant at this temperature. This aspect will be included in the discussion of the problem results.

²⁰D. R. Stull and H. Prophet, Project Directors, *JANAF Thermochemical Tables*, 2nd ed., NSRDS-NBS 37 (Washington, D.C.: U.S. Government Printing Office, 1971).

For rate constants, the data of Eklund²¹ can be correlated very well by the equation

$$k = \exp \left[\frac{-176,008}{T} - (110.1 \ln T) + 912.8 \right] \quad (\text{E8-10.2})$$

where k is in lb mol SO₂/lb cat · s · atm and T is in R.

There are diffusional effects present in this catalyst at these temperatures, and Equation (E8-10.2) should be regarded as an empirical equation that predicts the effective reaction rate constant over the range of temperatures listed by Donovan (814 to 1138°F). The JANAF tables were used to give the following:

$$\Delta H_{R_x}(800^\circ\text{F}) = -42,471 \text{ Btu/lb mol SO}_2 \quad (\text{E8-10.3})$$

$$C_{p_{\text{SO}_2}} = 7.208 + 5.633 \times 10^{-3} T - 1.343 \times 10^{-6} T^2 \quad (\text{E8-10.4})$$

$$C_{p_{\text{O}_2}} = 5.731 + 2.323 \times 10^{-3} T - 4.886 \times 10^{-7} T^2 \quad (\text{E8-10.5})$$

$$C_{p_{\text{SO}_3}} = 8.511 + 9.517 \times 10^{-3} T - 2.325 \times 10^{-6} T^2 \quad (\text{E8-10.6})$$

$$C_{p_{\text{N}_2}} = 6.248 + 8.778 \times 10^{-4} T - 2.13 \times 10^{-8} T^2 \quad (\text{E8-10.7})$$

where C_p is in Btu/lb mol · °R and T in °R.

Solution

1. General procedure:

- Apply the *plug-flow design equation* relating catalyst weight to the rate of reaction and conversion. Use stoichiometric relationships and feed specifications to express the rate law as a function of conversion.
- Apply the *energy balance* relating catalyst weight and temperature.
- Using the *Ergun equation* for pressure drop, determine the pressure as a function of catalyst weight.
- State *property values* [e.g., k , K_p , $\Delta H_{R_x}(T_R)$, C_{pi}] and their respective temperature dependences necessary to carry out the calculations.
- Numerically integrate* the design equation, energy balance, and Ergun equation simultaneously to determine the exit conversion and the temperature and concentration profiles.

- Design equations.** The general mole balance equations (design equations) based on the weight of catalyst were given in their differential and integral forms by

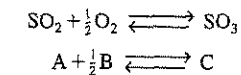
$$F_{A0} \frac{dX}{dW} = -r'_A$$

3. Rate law:

$$-r'_{\text{SO}_2} = k \sqrt{\frac{P_{\text{SO}_2}}{P_{\text{SO}_3}}} \left[P_{\text{O}_2} - \left(\frac{P_{\text{SO}_3}}{K_p P_{\text{SO}_2}} \right) \right]$$

²¹R. B. Eklund, as quoted by J. R. Donovan, in W. W. Duecker and J. R. West, *The Manufacture of Sulfuric Acid* (New York: Reinhold, 1959).

4. Stoichiometric relationships and expressing $-r'_{\text{SO}_2}$ as a function of X :



We let A represent SO₂ and ν_i the stoichiometric coefficient for species i :

$$P_i = C_i(RT) = C_{A0} \frac{(\Theta_i + \nu_i X)(RT)P}{(1 + \varepsilon X)(T/T_0)P_0} = P_{A0} \frac{(\Theta_i + \nu_i X)P}{(1 + \varepsilon X)P_0} \quad (\text{E8-10.8})$$

Substituting for partial pressures in the rate law and combining yields

$$\frac{dX}{dW} = \frac{-r'_A}{F_{A0}} = \frac{k}{F_{A0}} \sqrt{\frac{1-X}{\Theta_{\text{SO}_3} + X}} \left[\frac{P}{P_0} P_{A0} \frac{\Theta_{\text{O}_2} - \frac{1}{2}X}{1 + \varepsilon X} - \left(\frac{\Theta_{\text{SO}_3} - X}{1 + X} \right) \frac{1}{K_p} \right] \quad (\text{E8-10.9})$$

where $\varepsilon = -0.055$, $P_{A0} = 0.22$ atm, $\Theta_{\text{SO}_2} = 1.0$, $\Theta_{\text{O}_2} = 0.91$, $\Theta_{\text{SO}_3} = 0.0$, and $\Theta_{\text{N}_2} = 7.17$; $F_{T0} = 7900$ lb mol/h, and $F_{A0} = 869$ lb mol/h.

Per tube:

Weight of catalyst in one tube = $W = \rho_b \pi D^2 / 4 L = 28.54$ lb cat./tube

$$F_{A0} = \frac{869}{4631} = 0.188 \text{ lb mol/h} \cdot \text{tube}$$

Substituting the values above gives us

$$\frac{dX}{dW} = \frac{-r'_A}{F_{A0}} = 5.32k \sqrt{\frac{1-X}{X}} \left\{ \left(\frac{0.2 - 0.11X}{1 - 0.055X} \right) \frac{P}{P_0} - \left[\frac{X}{(1-X)K_p} \right] \right\} \quad (\text{E8-10.10})$$

that is,

$$\frac{dX}{dW} = f_1(X, T, P) \quad (\text{E8-10.11})$$

The limits of integration are from zero to the weight of catalyst in one tube, 28.54 lb.

- Energy balance.** For steady-state operation and no shaft work, Equation (8-56) can be rewritten in terms of catalyst weight as the spatial variable, that is,

$$\frac{dT}{dW} = \frac{(4U/\rho_b D)(T_a - T) + (-r'_A)[- \Delta H_{R_x}(T)]}{F_{A0}(\sum \Theta_i C_{pi} + X \Delta C_p)} \quad (\text{E8-10.12})$$

6. Evaluating the energy balance parameters:

Heat of reaction:

$$\Delta H_{R_x}(T) = \Delta H_{R_x}^\circ(T_R) + \Delta \alpha(T - T_R) + \frac{\Delta \beta}{2}(T^2 - T_R^2) + \frac{\Delta \gamma}{3}(T^3 - T_R^3) \quad (\text{E8-10.13})$$

For the SO_2 oxidation, $\text{SO}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{SO}_3$,

$$\Delta\alpha = \alpha_{\text{SO}_3} - \frac{1}{2}\alpha_{\text{O}_2} - \alpha_{\text{SO}_2} = 8.511 - (0.5)(5.731) - 7.208 = -1.563$$

Similarly,

$$\Delta\beta = 0.00262 \quad \text{and} \quad \Delta\gamma = -0.738 \times 10^{-6}$$

Substituting into Equation (E8-10.13) with $T_R = 1260^\circ\text{R}$, we have

$$\Delta H_{\text{Rx}}(T) = -42,471 - (1.563)(T - 1260) + (1.36 \times 10^{-3})(T^2 - 1260^2) - (2.459 \times 10^{-7})(T^3 - 1260^3) \quad (\text{E8-10.14})$$

$$\sum \Theta_i C_{pi} = 57.23 + 0.014T - 1.94 \times 10^{-6}T^2 \quad (\text{E8-10.15})$$

Heat-transfer coefficient term:

$$\begin{aligned} \frac{U\pi D}{\rho_b A_c} &= \frac{4U}{\rho_b D} = \frac{4(10 \text{ Btu/h} \cdot \text{ft}^2 \cdot ^\circ\text{R})}{(33.8 \text{ lb/ft}^3)(2.78/12) \text{ ft}} \\ &= 5.11 \text{ Btu/h} \cdot \text{lb cat} \cdot \text{R} \end{aligned}$$

$$\frac{dT}{dW} = \frac{5.11(T_a - T) + (-r'_A)[- \Delta H_{\text{Rx}}(T)]}{0.188(\sum \Theta_i C_{pi} + X \Delta C_p)} \quad (\text{E8-10.16})$$

that is,

$$\frac{dT}{dW} = f_2(T, P, X) \quad (\text{E8-10.17})$$

7. **Pressure drop:** After rearranging Equation (4-23), the pressure drop is given by

$$\frac{dP}{dz} = - \frac{(1 - \phi)G(1 + \varepsilon X)}{\rho_0(P/P_0)(T_0/T)g_c D_p \phi^3} \left[\frac{150\mu(1 - \phi)}{D_p} + 1.75G \right]$$

where

$$\begin{aligned} G &= \frac{\sum F_{i0} M_i}{A_c} \quad (M_i = \text{molecular weight of } i) \\ &= 1307.6 \text{ lb/ft}^2 \cdot \text{h} \\ A_c &= \text{cross-sectional area } \pi D^2/4 \end{aligned}$$

Recalling that $W = \rho_b A_c z$, we obtain

$$\frac{dP}{dW} = - \frac{GTP_0(1 - \phi)(1 + \varepsilon X)}{\rho_b A_c \rho_0 T_0 P D_p g_c \phi^3} \left[\frac{150(1 - \phi)\mu}{D_p} + 1.75G \right] \quad (\text{E8-10.18})$$

8. **Evaluating the pressure-drop parameters:**

$$f_3(X, T, P) = - \frac{GTP_0(1 - \phi)(1 + \varepsilon X)}{\rho_b A_c \rho_0 T_0 \phi^3 D_p g_c P} \left[\frac{150(1 - \phi)\mu}{D_p} + 1.75G \right] \quad (\text{E8-10.19})$$

Back-of-the-envelope calculation for ΔP

The coupled differential equations to be solved with an ODE solver

Substituting in Equation (E8-10.18), we get

$$\frac{dP}{dW} = \frac{-1.12 \times 10^{-8}(1 - 0.55X)T}{P} (5500\mu + 2288) \quad (\text{E8-10.20})$$

We wish to obtain an order-of-magnitude estimate of the pressure drop. To obtain this estimate, we consider the reaction to be carried out isothermally with $\varepsilon = 0$,

$$\frac{dP}{dW} = \frac{-0.0432}{P}$$

Integrating with limits $P_0 = 2 \text{ atm}$ at $W = 0$ and $P = P$ at $W = 28.54 \text{ lb of catalyst yields}$

$$\frac{P^2 - 4}{2} = -0.0432(0 - 28.54)$$

$$P = 1.239 \text{ atm}$$

$$\Delta P = 2 - 1.24 = 0.76 \text{ atm}$$

Because the gas-phase viscosity is a weakly varying function of temperature (i.e., $\mu \sim \sqrt{T}$), we shall consider viscosity to be independent of temperature:

$$\frac{dP}{dW} = f_3(T, P, X) \quad (\text{E8-10.21})$$

9. **Solution procedure.** There are three coupled differential equations that must be solved simultaneously:

$$\text{Mole balance:} \quad \frac{dX}{dW} = f_1(T, P, X) \quad (8-10.11)$$

$$\text{Energy balance:} \quad \frac{dT}{dW} = f_2(T, P, X) \quad (8-10.17)$$

$$\text{Momentum balance:} \quad \frac{dP}{dW} = f_3(T, P, X) \quad (8-10.21)$$

10. **Numerical procedure.** The rate equation is independent of conversion between $X = 0.0$ and $X = 0.05$ and the rate of disappearance of SO_2 over this range is equal to the rate of reaction at $X = 0.05$:

$$-r'_{\text{SO}_2} = k \left(0.848 - \frac{0.012}{K_p} \right) \quad (\text{E8-10.22})$$

- Set $X = 0.00$, $T = T_0$, and $P = P_0$.
- Calculate k from Equation (E8-10.2).
- Calculate K_p from Equation (E8-10.1).
- If $X < 0.05$, calculate $-r'_{\text{SO}_2}$ from Equation (E8-10.22). If $X > 0.05$, use Equation (E8-10.10).
- Calculate X , T , and P from a numerical solution to Equations (E8-10.10), (E8-10.16) and (E8-10.20).

The POLYMATH program is given in Table E8-10.1.

TABLE E8-10.1. SO₃ OXIDATION POLYMATH PROGRAM

Equations:	Initial Values:
$d(P)/d(w) = (-1.12 \times 10^{10} \cdot (-8) \cdot (1 - .055 \cdot x) \cdot T) \cdot (5500 \cdot \text{visc} + 2288) / P$	2
$d(x)/d(w) = (-r_a) / f_{ao}$	0
$d(T)/d(w) = (5.11 \cdot (T_a - T) + (-r_a) \cdot (-\Delta H)) / (f_{ao} \cdot (\sum x \cdot dcp))$	1400
$f_{ao} = .188$	
$\text{visc} = .090$	
$T_a = 1264.67$	
$\Delta H = -42471 - 1.563 \cdot (T - 1260) + .00136 \cdot (T^2 - 1260^2) - 2.459 \cdot 10^5 \cdot (-7) \cdot (T^3 - 1260^3)$	
$\text{sum} = 57.23 + .014 \cdot T - 1.94 \cdot 10^{-6} \cdot T^2$	
$dcp = -1.5625 + 2.72 \cdot 10^{-3} \cdot T - 7.38 \cdot 10^{-7} \cdot T^2$	
$k = 3600 \cdot \exp(-176008/T - (110.1 \cdot \ln(T)) + 912.8)$	
$\theta_{aso} = 0$	
$P_o = 2$	
$P_{ao} = .22$	
$\theta_{tao} = .91$	
$\epsilon_p = -.055$	
$R = 1.987$	
$K_p = \exp(42311/R/T - 11.24)$	
$r_a = \text{if}(x = .05) \text{ then } (-k \cdot (.848 - .012/(K_p^2))) \text{ else } (-k \cdot ((1-x)/(\theta_{aso} + x)) \cdot .5 \cdot (P/P_o \cdot P_{ao} \cdot ((\theta_{tao} - .5 \cdot x)/(1 + \epsilon_p \cdot x)) - ((\theta_{tao} + x)/(1-x))^2 / (K_p^2)))$	
$w_0 = 0, \quad w_f = 28.54$	

11. **Discussion of results.** Figure E8-10.1 shows the profiles for inlet temperatures of 1200°R and 1400°R, respectively. Only 68.5% conversion is achieved for $T_0 = 1200^\circ\text{R}$, even though $X_e = 0.99$. For an entering temperature of 1400°R, the major portion of the reaction takes place in the first 6 ft of the reactor. At this point, the conversion is 0.81, with only another 0.06 of the conversion occurring in the remaining 14 ft, as shown in Figure E8-10.1b. The cause of this low amount of conversion in the final 14 ft is the steadily dropping temperature in the reactor. Beyond the 6-ft point, the temperature is too low for much reaction to take place, which means that the reactor is cooled too much.

This detrimental situation indicates that the coolant temperature is too low for obtaining maximum conversion. Thus even boiling Dowtherm A at its highest possible operating temperature is not a suitable coolant. Perhaps a gas would give a better performance as a coolant in this reaction system. Two problems at the end of the chapter pursue this aspect. One of them seeks the optimum coolant temperature for a constant-coolant-temperature system, and the other uses inlet gas as a coolant.

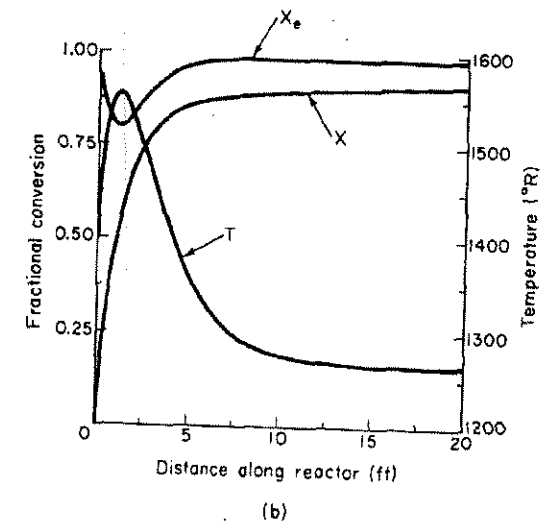
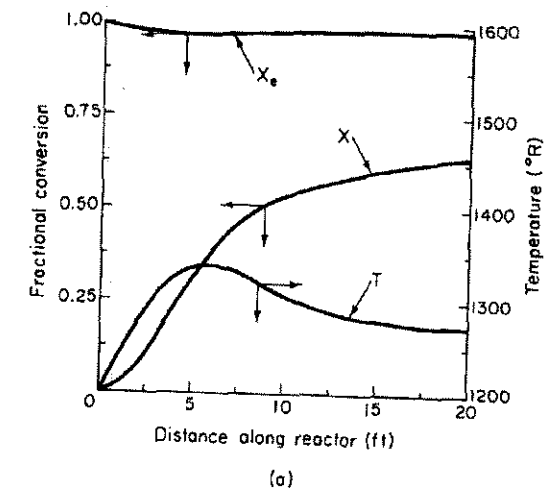


Figure E8-10.1 Conversion, temperature, and equilibrium conversion profiles within the reactor: (a) inlet temperature at 1200°R; (b) inlet temperature at 1400°R.

Analyzing the
effects of pressure
drop

Another possible way to operate such a reactor is to use multiple-stage operation with progressively higher coolant temperatures. Because pressure drop over the reactor is small (~ 0.7 atm), neglecting the pressure drop does not affect the exit conversion significantly (Figure 8-17). The effect is more significant at lower reactor inlet temperatures because the rate of reaction is appreciable over a longer portion of the reactor bed. At higher inlet temperatures the conversion is limited by the approach to equilibrium, and hence the pressure drop has a negligible effect.

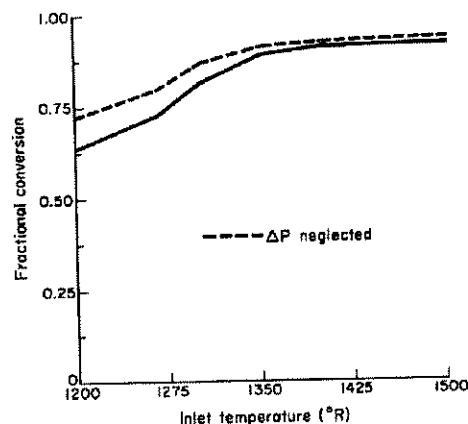


Figure 8-17 Fractional conversion as a function of reactor inlet temperature.

8.6 Multiple Steady States

In this section we consider the steady-state operation of a CSTR in which a first-order reaction is taking place. We begin by recalling the hydrolysis of propylene oxide, Example 8-4.

If one were to examine Figure E8-4.2, one would observe that if a parameter were changed slightly, there might be more than one intersection of the energy and mole balance curves. When more than one intersection occurs, there is more than one set of conditions that satisfy both the energy balance and mole balance, and consequently there will be multiple steady states at which the reactor may operate.

Neglecting shaft work in the CSTR, and setting $\Delta\hat{C}_p = 0$, [i.e., for $\Delta\hat{C}_p = 0$, $\Delta H_{R_x}^\circ(T) = \Delta H_{R_x}^\circ(T_R) = \Delta H_{R_x}^\circ$] the energy balance [Equation (8-51)] can be rearranged in the form

$$-F_{A0}X \Delta H_{R_x}^\circ(T) = F_{A0} \left[\sum \Theta_i \tilde{C}_{pi}(T - T_0) + \frac{UA}{F_{A0}}(T - T_a) \right] \quad (8-64)$$

Substituting the mole balance on a CSTR,

$$F_{A0}X = -r_A V \quad (2-12)$$

into Equation (8-64) gives

$$(-r_A V)(-\Delta H_{R_x}) = F_{A0}C_{p0}(T - T_0) + UA(T - T_a) \quad (8-65)$$

where

$$C_{p0} = \sum \Theta_i \tilde{C}_{pi}$$

By letting

$$\kappa = \frac{UA}{C_{p0}F_{A0}}$$

and

$$T_c = \frac{T_0 F_{A0} C_{p0} + UA T_a}{UA + C_{p0} F_{A0}} = \frac{\kappa T_a + T_0}{1 + \kappa} \quad (8-66)$$

Equation (8-65) may be simplified to

$$(-r_A V / F_{A0})(-\Delta H_{R_x}^\circ) = C_{p0}(1 + \kappa)(T - T_c) \quad (8-67)$$

The left-hand side is referred to as the *heat-generated term*:

$G(T)$ = heat-generated term

$$G(T) = (-\Delta H_{R_x}^\circ)(-r_A V / F_{A0}) \quad (8-68)$$

The right-hand side of Equation (8-67) is referred to as the *heat-removed term* (by flow and heat exchange) $R(T)$:

Heat-removed term

$$R(T) = C_{p0}(1 + \kappa)(T - T_c) \quad (8-69)$$

To study the multiplicity of steady states, we shall plot both $R(T)$ and $G(T)$ as a function of temperature on the same graph and analyze the circumstances under which we will obtain multiple intersections.

8.6.1 Heat-Removed Term, $R(T)$

From Equation (8-69) we see that $R(T)$ increases linearly with temperature, with slope $C_{p0}(1 + \kappa)$. As the entering temperature T_0 is increased, the line retains the same slope but shifts to the right as shown in Figure 8-18.

If one increases κ by either decreasing the molar flow rate F_{A0} or increasing the heat-exchange area, the slope increases and the ordinate intercept moves to the left as shown in Figure 8-19, for conditions of $T_a < T_0$:

$$\kappa = 0 \quad T_c = T_0$$

$$\kappa = \infty \quad T_c = T_a$$

If $T_a > T_0$, the intercept will move to the right as κ increases.

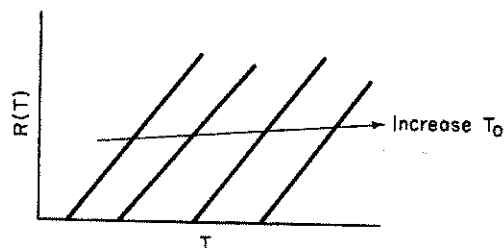
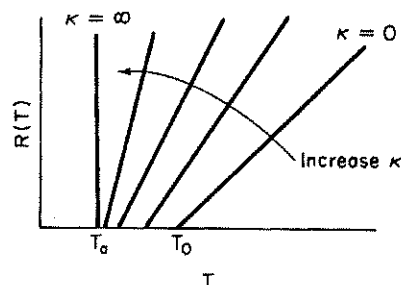
Heat-removed curve
 $R(T)$ 

Figure 8-18 Variation of heat removal line with inlet temperature.

$$\kappa = \frac{UA}{C_{p0}F_{A0}}$$

$$T_c = \frac{T_0 + \kappa T_a}{1 + \kappa}$$

Figure 8-19 Variation of heat removal line with κ ($\kappa = UA/C_{p0}F_{A0}$).8.6.2 Heat of Generation, $G(T)$

The heat-generated term, Equation (8-68), can be written in terms of conversion, (recall: $X = -r_A V/F_{A0}$)

$$G(T) = (-\Delta H_{Rx}^\circ)X \quad (8-70)$$

To obtain a plot of heat generated, $G(T)$, as a function of temperature, we must solve for X as a function of T using the CSTR mole balance, the rate law, and stoichiometry. For example, for a first-order liquid-phase reaction, the CSTR mole balance becomes

$$V = \frac{F_{A0}X}{kC_A} = \frac{v_0 C_{A0}X}{kC_{A0}(1-X)}$$

Solving for X yields

1st order reaction

$$X = \frac{\tau k}{1 + \tau k}$$

Substituting for X in Equation (8-70), we obtain

$$G(T) = \frac{-\Delta H_{Rx}^\circ \tau k}{1 + \tau k} \quad (8-71)$$

Finally, substituting for k in terms of the Arrhenius equation, we obtain

$$G(T) = \frac{-\Delta H_{Rx}^\circ \tau A e^{-E/RT}}{1 + \tau A e^{-E/RT}} \quad (8-72)$$

Note that equations analogous to Equation (8-71) for $G(T)$ can be derived for other reaction orders and for reversible reactions simply by solving the CSTR mole balance for X . For example, for the second-order liquid-phase reaction

2nd order reaction

$$X = \frac{(2\tau k C_{A0} + 1) - \sqrt{4\tau k C_{A0} + 1}}{2\tau k C_{A0}}$$

and the corresponding heat generated is

$$G(T) = \frac{-\Delta H_{Rx}^\circ [(2\tau C_{A0} A e^{-E/RT} + 1) - \sqrt{4\tau C_{A0} A e^{-E/RT} + 1}]}{2\tau C_{A0} A e^{-E/RT}} \quad (8-73)$$

At very low temperatures, the second term in the denominator of Equation (8-72) can be neglected, so that $G(T)$ varies as

Low T

$$G(T) = -\Delta H_{Rx}^\circ \tau A e^{-E/RT}$$

(Recall ΔH_{Rx}° means the heat of reaction is evaluated at T_R .)

At very high temperatures, the second term in the denominator dominates and $G(T)$ is reduced to

High T

$$G(T) = -\Delta H_{Rx}^\circ$$

$G(T)$ is shown as a function of T for two different activation energies, E_A , in Figure 8-20. If the flow rate is decreased or the reactor volume increased so as to increase τ , the heat of generation term, $G(T)$, changes as shown in Figure 8-21.

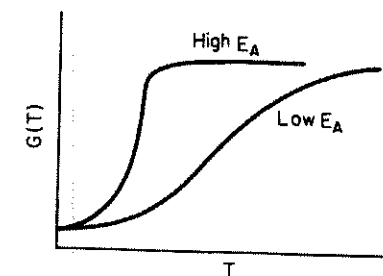


Figure 8-20 Heat generation curve.

8.6.3 Ignition-Extinction Curve

The points of intersection of $R(T)$ and $G(T)$ give us the temperature at which the reactor can operate at steady state. Suppose that we begin to feed our reactor at some relatively low temperature, T_{01} . If we construct our $G(T)$ and

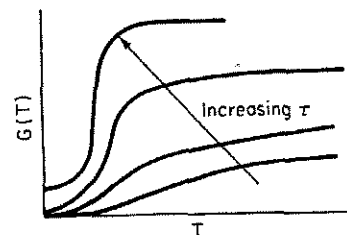
Heat-generated
curves, $G(T)$ 

Figure 8-21 Variation of heat generation curve with space-time.

$R(T)$ curves, illustrated by curves y and a , respectively, in Figure 8-22, we see that there will be only one point of intersection, point 1. From this point of intersection, one can find the steady-state temperature in the reactor, T_{s1} , by following a vertical line to the T axis and reading off the temperature as shown in Figure 8-22.

If one were now to increase the entering temperature to T_{02} , the $G(T)$ curve would remain unchanged but the $R(T)$ curve would move to the right, as shown by line b in Figure 8-22, and will now intersect the $G(T)$ at point 2 and be tangent at point 3. Consequently, we see from Figure 8-22 that there are two steady-state temperatures, T_{s2} and T_{s3} , that can be realized in the CSTR for an entering temperature T_{02} . If the entering temperature is increased to T_{03} , the $R(T)$ curve, line c (Figure 8-23), intersects the $G(T)$ three times and there are three steady-state temperatures. As we continue to increase T_0 , we finally reach line e , in which there are only two steady-state temperatures. By further increasing T_0 we reach line f , corresponding to T_{06} , in which we have only one temperature that will satisfy both the mole and energy balances. For the six entering temperatures, we can form Table 8-4, relating the entering temperature to the

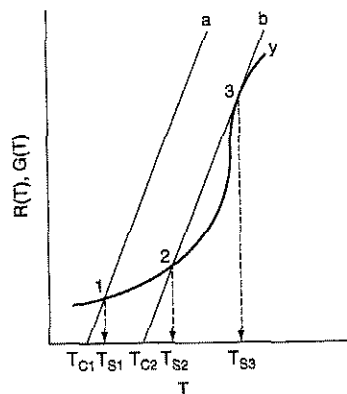
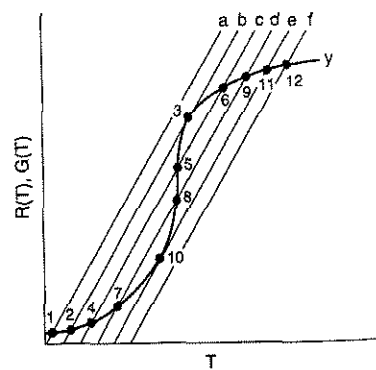
Both the mole and
energy balances are
satisfied at the
points of
intersection or
tangencyFigure 8-22 Finding multiple steady states with T_0 varied.Figure 8-23 Finding multiple steady states with T_0 varied.

TABLE 8-4. MULTIPLE STEADY-STATE TEMPERATURES

Entering Temperature	Reactor Temperatures					
T_{01}			T_{s1}			
T_{02}		T_{s2}		T_{s3}		
T_{03}	T_{s4}		T_{s5}		T_{s6}	
T_{04}	T_{s7}		T_{s8}		T_{s9}	
T_{05}		T_{s10}		T_{s11}		
T_{06}			T_{s12}			

We must exceed a certain feed temperature to operate at the upper steady state where the temperature and conversion are higher

possible reactor operating temperatures. By plotting T_s as a function of T_0 , we obtain the well-known *ignition-extinction curve* shown in Figure 8-24. From this figure we see that as the entering temperature is increased, the steady-state temperature increases along the bottom line until T_{05} is reached. Any fraction of a degree increase in temperature beyond T_{05} and the steady-state reactor temperature will jump up to T_{s11} , as shown in Figure 8-24. The temperature at which this jump occurs is called the *ignition temperature*. If a reactor were operating at T_{s12} and we began to cool the entering temperature down from T_{06} , the steady-state reactor temperature T_{s3} would eventually be reached, corresponding to an entering temperature T_{02} . Any slight decrease below T_{02} would drop the steady-state reactor temperature to T_{s2} . Consequently, T_{02} is called the *extinction temperature*.

The middle points 5 and 8 in Figures 8-23 and 8-24 represent unstable steady-state temperatures. For example, if by some means one were operating at T_{s5} and a pulse increase in the temperature suddenly occurred, the heat gener-

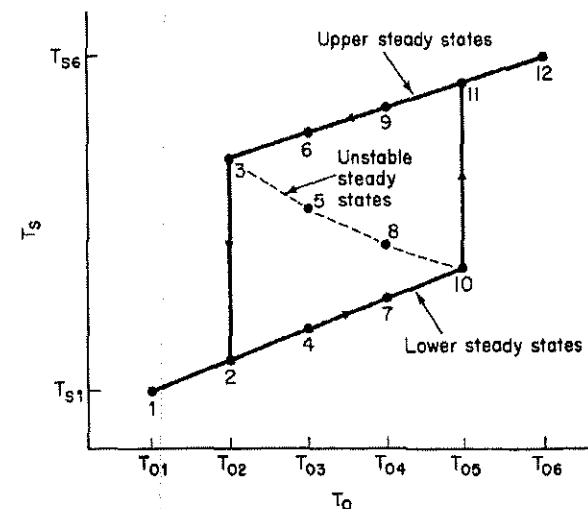


Figure 8-24 Temperature ignition-extinction curve.

Not all the multiple steady states are stable

ated would be greater than the heat removed and the steady-state reactor temperature would continue to increase until temperature T_{s6} was reached. On the other hand, if a sudden pulse decrease in temperature occurred at T_{s5} , the heat removed $R(T)$ would be greater than the heat generated $G(T)$ and the steady-state reactor temperature would continue to fall until T_{s4} was reached. Steady-state conditions that behave in this manner are said to be unstable.

In contrast to these unstable operating points, consider what would happen to the reactor temperature if a reactor operating at T_{s12} were subjected to very small temperature fluctuations. From Figure 8-24 we observe that a pulse increase in reactor temperature would make the heat of removal greater than the heat of generation [the $R(T)$ curve would be above the $G(T)$ curve] and the temperature would drop back down to T_{s12} . If a small pulse decrease in the reactor temperature occurred while the feed temperature remained constant at T_{06} , we would see that the curve $G(T)$ would be above the heat-removed curve $R(T)$ and the reactor temperature would continue to rise until T_{s12} was again reached. A similar analysis could be carried through for reactor temperatures T_{s1} , T_{s2} , T_{s4} , T_{s6} , T_{s7} , T_{s9} , T_{s11} , and T_{s12} and one would find that when these reactor temperatures are subjected to either a small positive or negative fluctuation, they will always return to their local steady-state values. Consequently, we say that these points are *locally stable steady states*. While these points are locally stable, they are not necessarily globally stable. That is, a perturbation in temperature or concentration, while small, may be sufficient to cause the reactor to fall from the

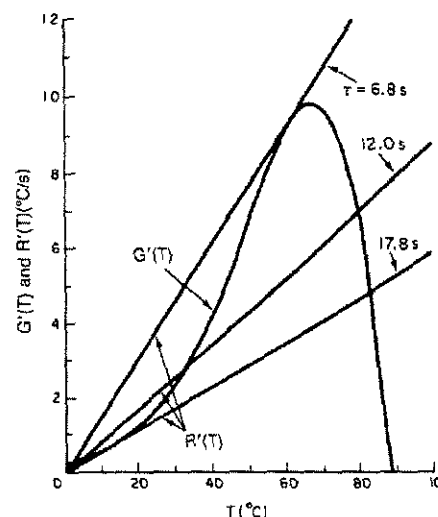
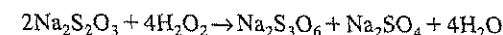


Figure 8-25 Heat generation and removal functions for feed mixture of 0.8 M $\text{Na}_2\text{S}_2\text{O}_3$ and 1.2 M H_2O_2 at 0°C . By S. A. Vejtasa and R. A. Schmitz, *AIChE J.*, 16(3), 415, (1970). (Reproduced by permission of the American Institute of Chemical Engineers. Copyright © 1970 AIChE. All right reserved.) See Problem P8C-4.

upper steady state (corresponding to high conversion and temperature) to the lower steady state (corresponding to low temperature and conversion). We will examine this case in detail in Section 9.4 and in Problem P9-15.

An excellent experimental investigation that demonstrates the multiplicity of steady states was carried out by Vejtasa and Schmitz. (Figure 8-25)²² They studied the reaction between sodium thiosulfate and hydrogen peroxide:



in a CSTR operated adiabatically. The multiple steady-state temperatures were examined by varying the flow rate over a range of space times, τ , as shown in Figure 8-26. One observes from this figure that at a space-time of 12 s, steady-state reaction temperatures of 4, 33, and 80°C are possible. If one were operating on the higher steady-state temperature line and the volumetric flow rates were steadily increased (i.e., the space-time decreased), one notes that if the space velocity dropped below about 7 s, the reaction temperature would drop from 70°C to 2°C . The flow rate at which this drop occurs is referred to as the *blowout velocity*.

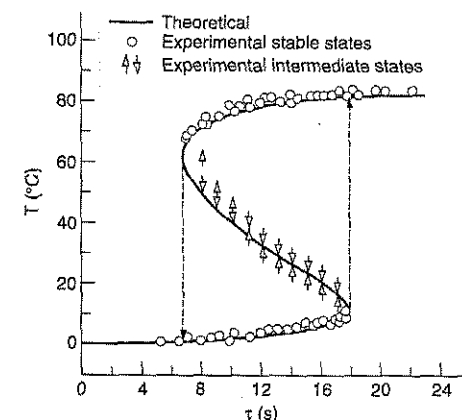


Figure 8-26 Multiple steady states.

8.6.4 Runaway Reactions

In many reacting systems the temperature of the upper steady state may be sufficiently high that it is undesirable or even dangerous to operate at this condition. From Figure 8-24 we saw that once we exceed the ignition temperature, we will proceed to the upper steady state. The ignition temperature occurs at point 10 on Figure 8-23, which is a point of tangency of the heat-removed curve with

²²S. A. Vejtasa and R. A. Schmitz, *AIChE J.*, 16, 410 (1970).

the heat-generated curve. At this point of tangency the slopes of the $R(T)$ and $G(T)$ curves are equal. That is, for the heat removal curve we have

$$\frac{dR(T)}{dT} = C_{p0}(1 + \kappa) \quad (8-74)$$

and for the heat-generated curve

$$\frac{dG(T)}{dT} = \frac{d \left[(-\Delta H_{Rx}) \frac{-r_A V}{F_{A0}} \right]}{dT} = \frac{(-\Delta H_{Rx}) V}{F_{A0}} \frac{d(-r_A)}{dT}$$

Assuming that the reaction is irreversible, follows a power law model, and that the concentrations of the reacting species are weak functions of temperature,

$$-r_A = (Ae^{-E/RT}) \text{fn}(C_i)$$

then

$$\frac{d(-r_A)}{dT} = \frac{E}{RT^2} Ae^{-E/RT} \text{fn}(C_i) = \frac{E}{RT^2} (-r_A) \quad (8-75)$$

Equating Equations (8-74) and (8-75) yields

$$C_{p0}(1 + \kappa) = \frac{E}{RT^2} (-r_A) \frac{-\Delta H_{Rx} V}{F_{A0}} \quad (8-76)$$

Finally, we divide Equation (8-67) by Equation (8-76) to obtain the following ΔT value for a CSTR operating at $T = T_r$.

$$\Delta T_{rc} = T_r - T_c = \frac{RT_r^2}{E} \quad (8-77)$$

If this ΔT_{rc} is exceeded, transition to the upper steady state will occur. For many industrial reactions E/RT is typically between 16 and 24, and the reaction temperatures may be 300 to 500 K. Consequently, this critical temperature difference ΔT_{rc} will be somewhere around 15 to 30°C.

8.6.5 Steady-State Bifurcation Analysis

In reactor dynamics it is particularly important to find out if multiple stationary points exist or if sustained oscillations can arise. Bifurcation analysis is aimed at locating the set of parameter values for which multiple steady states will occur.²³ We apply bifurcation analysis to learn whether or not multiple steady states are possible. An outline of what is on the CD-ROM follows.

²³V. Balakotaiah and D. Luss, in *Chemical Reaction Engineering*, Boston ACS Symposium Series 196 (Washington, D.C.: American Chemical Society, 1982), p. 65; M. Golubitsky and B. L. Keyfitz, *Siam. J. Math. Anal.*, 11, 316 (1980); A. Uppal, W. H. Ray, and A. B. Poore, *Chem. Eng. Sci.*, 29, 967 (1974).

Bifurcation analysis will be applied to the CSTR mole and energy balances. First, Equations (8-68) and (8-69) are combined and the energy balance is written as

$$F(T) = C_{p0}(1 + \kappa)T - C_{p0}(1 + \kappa)T_c - G(T) \quad (8-78)$$

which is of the form

$$F(T) = \alpha T - \beta - G(T) \quad (8-79)$$

Similarly, the CSTR mole balance can be written as

$$\frac{C_A}{\tau} - \frac{C_{A0}}{\tau} - r_A(C_A) = 0 \quad (8-80)$$

which is of a similar nature for the energy balance,

$$F(C_A) = \alpha C_A - \beta - G(C_A) \quad (8-81)$$

Both CSTR energy and mole balances are of the form

$$F(y) = \alpha y - \beta - G(y) \quad (8-82)$$

The conditions for uniqueness are then shown to be those that satisfy the relationship

$$\max \left(\frac{\partial G}{\partial y} \right) < \alpha \quad (8-83)$$

For example, if we use energy balance in the form given by Equation (8-78) and use Equations (8-75) and (8-76) we would find the criteria for uniqueness (i.e. No Multiple Steady States (MMS)) is

$$\left(\frac{E}{RT^2} (r_A \Delta H_{Rx}) \frac{V}{F_{A0}} \right)_{\max} < C_{p0}(1 + \kappa)$$

Criteria for no MSS

However, if

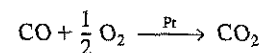
$$\max \left(\frac{\partial G}{\partial y} \right) > \alpha \quad (8-84)$$

we do not know if multiple steady solutions exist and we must carry the analysis further. Specifically, the conditions for which multiple steady states exist must satisfy the following set of equations:

$$(1) \quad \left. \frac{dF}{dy} \right|_{y^*} = 0 = \alpha - \left. \frac{dG}{dy} \right|_{y^*} \quad (8-85)$$

$$(2) \quad F(y^*) = 0 = \alpha y^* - \beta - G(y^*) \quad (8-86)$$

An example is given on the CD-ROM which maps out the regions where multiple steady states are possible and not possible for the reaction



with the rate law

$$-G(C_A) = -r_A = \frac{kC_A}{(1 + KC_A)^2}$$

A portion of the solution to the example problem is shown here (Figure CDE8-1.1), highlighting regions where multiple steady states are not possible.

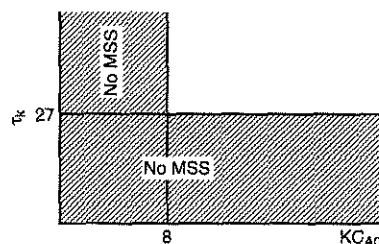


Figure CDE8-1.1 Mapping the regions of no multiple steady states.

8.7 Nonisothermal Multiple Chemical Reactions

8.7.1 Plug-Flow Reactors

In this section we give the energy balance for multiple reactions that are in parallel and/or in series. The energy balance for a single reaction taking place in a PFR was given by Equation (8-60)

$$\frac{dT}{dV} = \frac{Ua(T_a - T) + (-r_A)(-\Delta H_{Rx}(T))}{\sum_{i=1}^m F_i C_{pi}} \quad (8-60)$$

When q multiple reactions are taking place and there are m species, it is easily shown that Equation (8-60) can be generalized to

$$\frac{dT}{dV} = \frac{Ua(T_a - T) + \sum_{i=1}^q (-r_{ij})(-\Delta H_{Rxi}(T))}{\sum_{j=1}^m F_j C_{pj}} \quad (8-87)$$

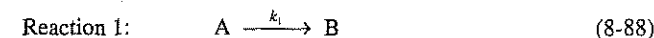
Energy balance for multiple reactions

The heat of reaction for reaction i must be referenced to the same species in the rate, r_{ij} , by which ΔH_{Rxi} is multiplied, that is,

$$[-r_{ij}][-\Delta H_{Rxi}] = \left[\frac{\text{moles of } j \text{ reacted in reaction } i}{\text{volume} \cdot \text{time}} \right] \times \left[\frac{\text{joules "released" in reaction } i}{\text{moles of } j \text{ reacted in reaction } i} \right] \\ = \left[\frac{\text{joules "released" in reaction } i}{\text{volume} \cdot \text{time}} \right]$$

where the subscript j refers to the species, the subscript i to the particular reaction, q is the number of **independent** reactions, and m is the number of species.

Consider the following reaction sequence carried out in a PFR:



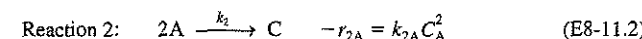
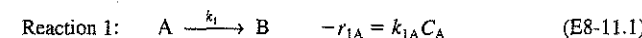
The PFR energy balance becomes

$$\frac{dT}{dV} = \frac{Ua(T_a - T) + (-r_{1A})(-\Delta H_{Rx1A}) + (-r_{2B})(-\Delta H_{Rx2B})}{F_A C_{pA} + F_B C_{pB} + F_C C_{pC}} \quad (8-90)$$

where ΔH_{Rx1A} = [kJ/mol of A reacted in reaction 1] and $[\Delta H_{Rx2B}$ = kJ/mol of B reacted in reaction 2].

Example 8-11 Parallel Reactions in a PFR with Heat Effects

The following gas-phase reactions occur in a PFR:



Pure A is fed at a rate of 100 mol/s, a temperature of 150°C and a concentration of 0.1 mol/dm³. Determine the temperature and flow rate profiles down the reactor.

Additional information:

$$\Delta H_{Rx1A} = \text{J/mol of A reacted in reaction 1} = -20,000 \text{ J/mol}$$

$$\Delta H_{Rx2A} = \text{J/mol of A reacted in reaction 2} = -60,000 \text{ J/mol}$$

$$C_{pA} = 90 \text{ J/mol} \cdot ^\circ\text{C} \quad k_{1A} = 10 \exp \left[\frac{E_1}{R} \left(\frac{1}{300} - \frac{1}{T} \right) \right] \text{ s}^{-1}$$

$$C_{pB} = 90 \text{ J/mol} \cdot ^\circ\text{C} \quad E_1 = 8000 \text{ cal/mol}$$

$$C_{pC} = 180 \text{ J/mol} \cdot ^\circ\text{C} \quad k_{2A} = 0.09 \exp \left[\frac{E_2}{R} \left(\frac{1}{300} - \frac{1}{T} \right) \right] \frac{\text{dm}^3}{\text{mol} \cdot \text{s}}$$

$$Ua = 4000 \text{ J/m}^3 \cdot \text{s} \cdot ^\circ\text{C} \quad E_2 = 18,000 \text{ cal/mol}$$

$$T_a = 100^\circ\text{C}$$

Solution

The PFR energy balance becomes (cf. Equation (8-87))

$$\frac{dT}{dV} = \frac{Ua(T_a - T) + (-r_{1A})(-\Delta H_{Rx1A}) + (-r_{2A})(-\Delta H_{Rx2A})}{F_A C_{pA} + F_B C_{pB} + F_C C_{pC}} \quad (\text{E8-11.3})$$

Mole balances:

$$\frac{dF_A}{dV} = r_{1A} + r_{2A} \quad (\text{E8-11.4})$$

$$\frac{dF_B}{dV} = -r_{1A} \quad (\text{E8-11.5})$$

$$\frac{dF_C}{dV} = -\frac{1}{2} r_{2A} \quad (\text{E8-11.6})$$

Rate laws:

$$C_A = C_{T0} \left(\frac{F_A}{F_T} \right) \left(\frac{T_0}{T} \right) \quad (\text{E8-11.7})$$

$$C_B = C_{T0} \left(\frac{F_B}{F_T} \right) \left(\frac{T_0}{T} \right) \quad (\text{E8-11.8})$$

$$C_C = C_{T0} \left(\frac{F_C}{F_T} \right) \left(\frac{T_0}{T} \right) \quad (\text{E8-11.9})$$

$$F_T = F_A + F_B + F_C \quad (\text{E8-11.10})$$

$$k_{1A} = 0.07 \exp \left[3000 \left(\frac{1}{300} - \frac{1}{T} \right) \right]$$

$$k_{2A} = 5.0 \exp \left[9000 \left(\frac{1}{300} - \frac{1}{T} \right) \right]$$

$$\frac{dT}{dV} = \frac{4000(375 - T) + (-r_{1A})(20,000) + (-r_{2A})(60,000)}{90F_A + 90F_B + 180F_C} \quad (\text{E8-11.11})$$

Stoichiometry (gas phase), $\Delta P = 0$:

$$r_{1A} = -k_{1A} C_A$$

$$r_{2A} = -k_{2A} C_A^2$$

The POLYMATH program and its graphical outputs are shown in Table E8-11.1 and Figures E8-11.1 and E8-11.2.

The algorithm for multiple reactions with heat effects

TABLE E8-11.1. POLYMATH PROGRAM

Equations:	Initial Values:
$d(F_B)/d(V) = -r_{1A}$	0
$d(F_A)/d(V) = r_{1A} + r_{2A}$	100
$d(F_C)/d(V) = -r_{2A}/2$	0
$d(T)/d(V) = (4000*(373-T) + (-r_{1A})*20000 + (-r_{2A})*60000) / (90*F_A + 90*F_B + 180*F_C)$	423
$k_{1A} = 10 * \exp(4000*(1/300 - 1/T))$	
$k_{2A} = 0.09 * \exp(9000*(1/300 - 1/T))$	
$C_{T0} = 0.1$	
$F_T = F_A + F_B + F_C$	
$T_0 = 423$	
$C_A = C_{T0} * (F_A/F_T) * (T_0/T)$	
$C_B = C_{T0} * (F_B/F_T) * (T_0/T)$	
$C_C = C_{T0} * (F_C/F_T) * (T_0/T)$	
$r_{1A} = -k_{1A} * C_A$	
$r_{2A} = -k_{2A} * C_A^2$	
$V_0 = 0, \quad V_f = 1$	

Why does the temperature go through a maximum value?

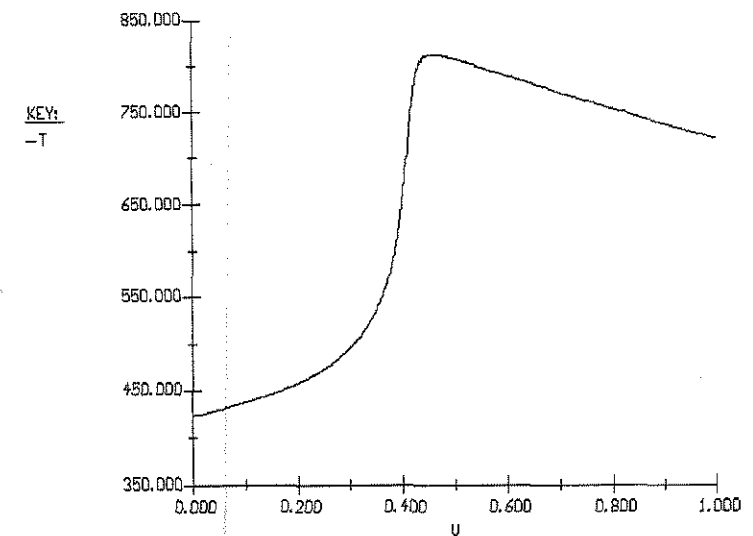
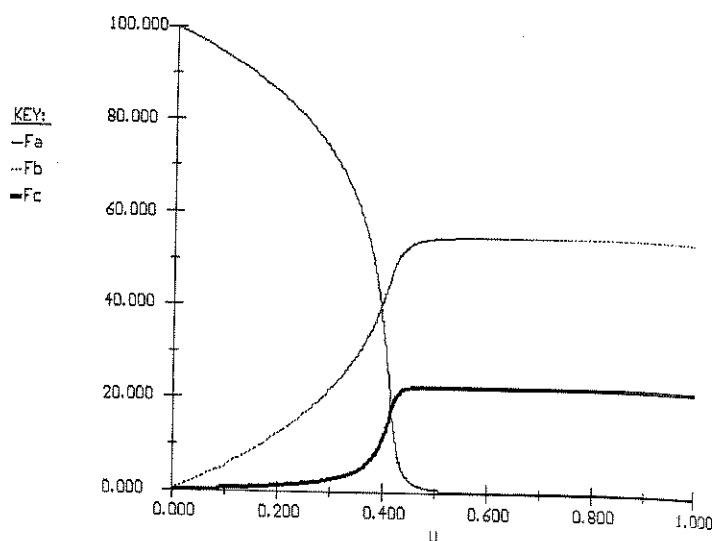


Figure E8-11.1 Temperature profile.

Figure E8-11.2 Profile of molar flow rates F_A , F_B , and F_C .

8.7.2 CSTR

For a CSTR, recall that $-F_{A0}X = r_A V$ and therefore the steady-state energy balance for a single reaction is

$$\dot{Q} - \dot{W}_s - F_{A0} \int_{T_0}^T \sum \Theta_i C_{pi} dT + \left[\Delta H_{Rx}^\circ(T_R) + \int_{T_R}^T \Delta C_p dT \right] [r_A V] = 0 \quad (8-48)$$

For q multiple reactions and m species, the CSTR energy balance becomes

$$\dot{Q} - \dot{W}_s - F_{A0} \int_{T_0}^T \sum \Theta_i C_{pi} dT + V \sum_{i=1}^q r_{ij} \Delta H_{Rxi}(T) = 0 \quad (8-91)$$

Energy Balance
For Multiple
Reactions in a
CSTR

Substituting Equation (8-42) for \dot{Q} , neglecting the work term, and assuming constant heat capacities, Equation (8-91) becomes

$$UA(T_a - T) - F_{A0} \sum C_{pi} \Theta_i (T - T_0) + V \sum_{i=1}^q r_{ij} \Delta H_{Rxi}(T) = 0 \quad (8-92)$$

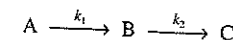
For the two parallel reactions described in Example 8-11, the CSTR energy balance is

$$UA(T_a - T) - F_{A0} \sum_{i=1}^m \Theta_i C_{pi} (T - T_0) + V r_{1A} \Delta H_{Rx1A}(T) + V r_{2A} \Delta H_{Rx2A}(T) = 0 \quad (8-92)$$

One of the major goals of this text is to have the reader solve problems involving multiple reactions with heat effects (cf. P8-30).

Example 8-12 Multiple Reactions in a CSTR

The elementary liquid-phase reactions



take place in a 10-dm³ CSTR. What are the effluent concentrations for a volumetric feed rate of 10 dm³/min at a concentration of A of 0.3 mol/dm³?

The inlet temperature is 283 K.

Additional information:

$$C_{PA} = C_{PB} = C_{PC} = 200 \text{ J/mol} \cdot \text{K}$$

$$k_1 = 3.03 \text{ min}^{-1} \text{ at } 300 \text{ K, with } E_1 = 9900 \text{ cal/mol}$$

$$k_2 = 4.58 \text{ min}^{-1} \text{ at } 500 \text{ K, with } E_2 = 27,000 \text{ cal/mol}$$

$$\Delta H_{Rx1A} = -55,000 \text{ J/mol A} \quad UA = 40,000 \text{ J/min} \cdot \text{K with } T_a = 57^\circ\text{C}$$

$$\Delta H_{Rx2B} = -71,500 \text{ J/mol B}$$

Solution

A: Combined mole balance and rate law for A:

$$V = \frac{v_0 (C_{A0} - C_A)}{k_1 C_A} \quad (E8-12.1)$$

Solving for C_A gives us

$$C_A = \frac{C_{A0}}{1 + \tau k_1} \quad (E8-12.2)$$

B: Combined mole balance and rate law for B:

$$V = \frac{0 - C_B v_0}{-r_B} = \frac{C_B v_0}{(r_{1B} + r_{2B})} = \frac{C_B v_0}{k_1 C_A - k_2 C_B} \quad (E8-12.3)$$

Solving for C_B yields

$$C_B = \frac{\tau k_1 C_A}{1 + \tau k_2} = \frac{\tau k_1 C_{A0}}{(1 + \tau k_1)(1 + \tau k_2)} \quad (E8-12.4)$$

Rate laws:

$$-r_{1A} = k_1 C_A = \frac{k_1 C_{A0}}{1 + \tau k_1} \quad (\text{E8-12.5})$$

$$-r_{2B} = k_2 C_B = \frac{k_2 \tau k_1 C_{A0}}{(1 + \tau k_1)(1 + \tau k_2)} \quad (\text{E8-12.6})$$

Applying Equation (8-92) to this system gives

$$UA(T_c - T) - F_{A0} \tilde{C}_{pA}(T - T_0) + V[r_{1A} \Delta H_{R1A} + r_{2B} \Delta H_{R2B}] = 0 \quad (\text{E8-12.7})$$

Substituting for r_{1A} and r_{2B} and rearranging, we have

$$\frac{G(T)}{R(T)} = \frac{C_p(1 + \kappa)[T - T_c]}{\left[-\frac{\Delta H_{R1A} \tau k_1}{1 + \tau k_1} - \frac{\tau k_1 \tau k_2 \Delta H_{R2B}}{(1 + \tau k_1)(1 + \tau k_2)} \right]} \quad (\text{E8-12.8})$$

$$\kappa = \frac{UA}{F_{A0} \tilde{C}_{pA}} = \frac{40,000 \text{ J/min} \cdot \text{K}}{(0.3 \text{ mol/dm}^3)(1000 \text{ dm}^3/\text{min}) 200 \text{ J/mol} \cdot \text{K}} = 0.667$$

$$T_c = \frac{T_0 + \kappa T_a}{1 + \kappa} = \frac{283 + (0.667)(330)}{1 + 0.667} = 301.8 \text{ K} \quad (\text{E8-12.9})$$

$$G(T) = \left[-\frac{\Delta H_{R1A} \tau k_1}{1 + \tau k_1} - \frac{\tau k_1 \tau k_2 \Delta H_{R2B}}{(1 + \tau k_1)(1 + \tau k_2)} \right] \quad (\text{E8-12.10})$$

$$R(T) = C_p(1 + \kappa)[T - T_c] \quad (\text{E8-12.11})$$

The POLYMATH program to plot $R(T)$ and $G(T)$ vs. T is shown in Table E8-12.1, and the resulting graph is shown in Figure E8-12.1.

TABLE E8-12.1. POLYMATH

Equations:	Initial Values:
$d(T)/d(t) = 2$	273
$C_p = 200$	
$C_{A0} = 0.3$	
$T_0 = 283$	
$\tau = 0.1$	
$DH1 = -55000$	
$DH2 = -71500$	
$v_0 = 1000$	
$E2 = 27000$	
$E1 = 9900$	
$UA = 40000$	
$T_a = 330$	
$k2 = 4.58 \cdot \exp((E2/1.987) \cdot (1/500 - 1/T))$	
$k1 = 3.3 \cdot \exp((E1/1.987) \cdot (1/300 - 1/T))$	
$Ca = C_{A0} / (1 + \tau \cdot k1)$	
$\kappa = UA / (v_0 \cdot C_{A0}) / C_p$	
$G = -\tau \cdot k1 / (1 + \tau \cdot k1) \cdot DH1 - \tau \cdot k1 \cdot \tau \cdot k2 \cdot \tau \cdot DH2 / ((1 + \tau \cdot k1) \cdot (1 + \tau \cdot k2))$	
$Tc = (T_0 + \kappa \cdot T_a) / (1 + \kappa)$	
$Ch = \tau \cdot k1 \cdot Ca / (1 + \tau \cdot k1)$	
$R = C_p \cdot (1 + \kappa) \cdot (T - Tc)$	
$Cc = C_{A0} - Ca - Ch$	
$F = G - R$	
$t_0 = 0, \quad t_f = 225$	

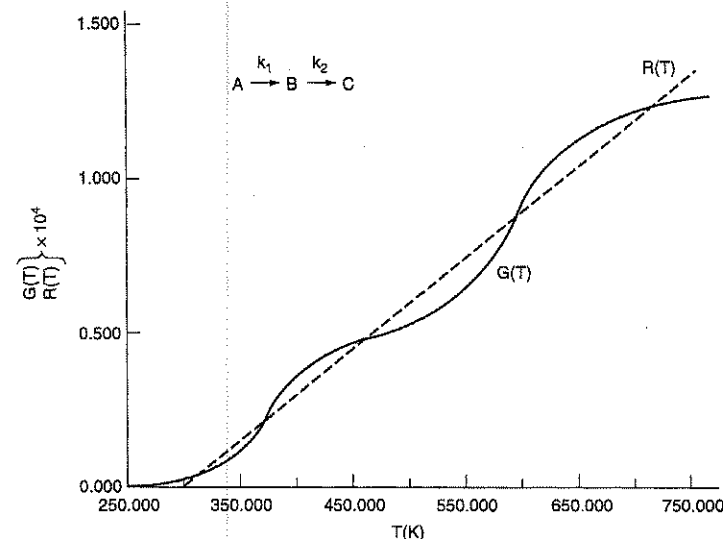


Figure E8-12.1 Heat-removed and heat-generated curves.

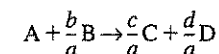
We see that five steady states (SS) exist. The exit concentrations and temperatures listed in Table E8-12.2 were interpreted from the tabular output of the POLYMATH program.

TABLE E8-12.2. EFFLUENT CONCENTRATIONS AND TEMPERATURES

SS	T	C_A	C_B	C_C
1	310	0.285	0.015	0
2	363	0.189	0.111	0.0
3	449	0.033	0.265	0.002
4	558	0.004	0.163	0.132
5	677	0.001	0.005	0.294

SUMMARY

For the reaction



1. The heat of reaction at temperature T , per mole of A, is

$$\Delta H_{RX}(T) = \frac{c}{a} H_C(T) + \frac{d}{a} H_D(T) - \frac{b}{a} H_B(T) - H_A(T) \quad (\text{S8-1})$$

2. The standard heat of reaction per mole of A at reference temperature T_R is given in terms of the heats of formation of each species:

$$\Delta H_{R,x}^\circ(T_R) = \frac{c}{a} H_C^\circ(T_R) + \frac{d}{a} H_D^\circ(T_R) - \frac{b}{a} H_B^\circ(T_R) - H_A^\circ(T_R) \quad (\text{S8-2})$$

3. The mean heat capacity difference, $\Delta \hat{C}_p$, per mole of A is

$$\Delta \hat{C}_p = \frac{c}{a} \hat{C}_{pC} + \frac{d}{a} \hat{C}_{pD} - \frac{b}{a} \hat{C}_{pB} - \hat{C}_{pA} \quad (\text{S8-3})$$

where \hat{C}_{pi} is the mean heat capacity of species i between temperatures T_R and T , not to be confused with C_{pi} , which is the mean heat capacity of species i between temperatures T_0 and T .

4. When there are no phase changes, the heat of reaction at temperature T is related to the standard reference heat of reaction by

$$\Delta H_{R,x}(T) = \Delta H_{R,x}^\circ(T_R) + \Delta \hat{C}_p(T - T_R) \quad (\text{S8-4})$$

5. Neglecting changes in potential energy, kinetic energy, and viscous dissipation, the steady-state energy balance is

$$\frac{\dot{Q}}{F_{A0}} - \frac{\dot{W}_s}{F_{A0}} - X[\Delta H_{R,x}^\circ(T) + \Delta \hat{C}_p(T - T_R)] = \sum_{i=1}^n \Theta_i \tilde{C}_{pi}(T - T_{i0}) \quad (\text{S8-5})$$

where n is the number of species entering the reactor.

If all species enter at the same temperature, $T_{i0} = T_0$, and no work is done on the system, the energy balance reduces to

$$\frac{\dot{Q}}{F_{A0}} - X[\Delta H_{R,x}^\circ(T) + \Delta \hat{C}_p(T - T_R)] = \left(\sum_{i=1}^n \Theta_i \tilde{C}_{pi} \right) (T - T_0) \quad (\text{S8-6})$$

For adiabatic operation of a PFR, PBR, CSTR, or batch reactor

$$T = \frac{X[-\Delta H_{R,x}^\circ(T_R) + \sum \Theta_i C_{pi} T_0 + X \Delta \hat{C}_p T_R]}{[\sum \Theta_i \tilde{C}_{pi} + X \Delta \hat{C}_p]}$$

6. The energy balance on a PFR/PBR

$$\frac{dT}{dV} = \frac{Ua(T_a - T) + (-r_A)[-\Delta H_{R,x}(T)]}{\sum_{i=1}^m F_i C_{pi}} \quad (\text{S8-7})$$

In terms of conversion

$$\frac{dT}{dV} = \frac{Ua(T_a - T) + (-r_A)[-\Delta H_{R,x}(T)]}{F_{A0}(\sum \Theta_i C_{pi} + X \Delta \hat{C}_p)} \quad (\text{S8-8})$$

7. The CSTR energy balance is

$$\frac{UA}{F_{A0}}(T_a - T) - X[\Delta H_{R,x}^\circ(T_R) + \Delta \hat{C}_p(T - T_R)] = \sum \Theta_i \tilde{C}_{pi}(T - T_{i0}) \quad (\text{S8-9})$$

8. The temperature dependence of the specific reaction rate is given in the form

$$k(T) = k_1(T_1) \exp \left[\frac{E}{R} \left(\frac{T - T_1}{TT_1} \right) \right] \quad (\text{S8-10})$$

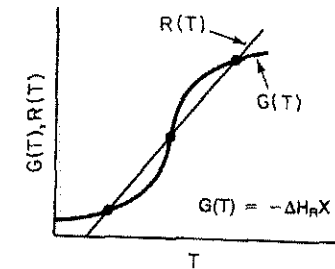
9. The temperature dependence of the equilibrium constant is given by van't Hoff's equation:

$$\frac{d \ln K_p}{dT} = \frac{\Delta H_{R,x}(T)}{RT^2}$$

If $\Delta C_p = 0$,

$$K_p(T) = K_p(T_1) \exp \left[\frac{\Delta H_{R,x}}{R} \left(\frac{1}{T_1} - \frac{1}{T} \right) \right] \quad (\text{S8-11})$$

10. Multiple steady states:



$$G(T) = (-\Delta H_{R,x}) \left(\frac{-r_A V}{F_{A0}} \right) = (-\Delta H_{R,x})(X) \quad (\text{S8-12})$$

$$R(T) = C_{p0}(1 + \kappa)(T - T_c) \quad (\text{S8-13})$$

For an irreversible first-order reaction,

$$G(T) = -\Delta H_{R,x} \frac{\tau A \exp(-E/RT)}{1 + \tau A \exp(-E/RT)}$$

11. The criteria for *Runaway Reactions* is when $(T_r - T_c) > RT_r^2/E$, where T_r is the reactor temperature and $T_c = (T_a + \kappa T_a)/(1 + \kappa)$.

12. Bifurcation analysis (CD-ROM) is used to find multiple steady states. At the bifurcation point, y^* ,

$$F(y^*) = 0 = \alpha y^* - \beta - G(y^*) \quad (\text{S8-14})$$

$$\left(\frac{dF}{dy} \right)_{y^*} = 0 = \alpha - \left. \frac{dG}{dy} \right|_{y^*} \quad (\text{S8-15})$$

Multiple steady states will not exist if

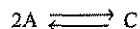
$$\max \left(\frac{dG}{dy} \right) < \alpha \quad (\text{S8-16})$$

13. When q multiple reactions are taking place and there are m species,

$$\frac{dT}{dV} = \frac{Ua(T_a - T) + \sum_{i=1}^q (-r_{ij})[-\Delta H_{R,ij}(T)]}{\sum_{j=1}^m F_j C_{pj}} \quad (\text{S8-17})$$

ODE SOLVER ALGORITHM

Packed-Bed Reactor with Heat Exchange and Pressure Drop



Pure A enters at 5 mol/min at 450 K.

$$\frac{dX}{dW} = \frac{-r'_A}{F_{A0}}$$

$$\frac{dT}{dW} = \frac{UA/\rho_c(T_a - T) + (r'_A)(\Delta H_{Rx})}{C_{pA}F_{A0}}$$

$$\frac{dy}{dW} = -\frac{\alpha}{2y} (1 - 0.5X)(T/T_0)$$

$$r'_A = -k[C_A^2 - C_C/K_C]$$

$$C_A = C_{A0}[(1 - X)/(1 - 0.5X)](T_0/T)$$

$$C_C = \frac{1}{2}C_{A0}X(T_0/T)/(1 - 0.5X)$$

$$k = 0.5 \exp[5032((1/450) - (1/T))]$$

$$K_C = 25,000 \exp\left[-10,065\left(\frac{1}{450} - \frac{1}{T}\right)\right]$$

$$\alpha = 0.019/\text{kg cat.}$$

$$C_{A0} = 0.25 \text{ mol/dm}^3$$

$$UA/\rho_c = 0.8 \text{ J/kg cat.} \cdot \text{s} \cdot \text{K}$$

$$T_a = 500 \text{ K}$$

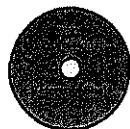
$$\Delta H_{Rx}^\circ = -20,000 \text{ J/mol}$$

$$C_{pA} = 40 \text{ J/mol} \cdot \text{K}$$

$$F_{A0} = 5.0 \text{ mol/s}$$

$$T_0 = 450 \text{ K}$$

$$W_t = 90 \text{ kg cat.}$$

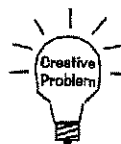


QUESTIONS AND PROBLEMS

The subscript to each of the problem numbers indicates the level of difficulty: A, least difficult; D, most difficult.

$$A = \bullet \quad B = \blacksquare \quad C = \blacklozenge \quad D = \blacklozenge\blacklozenge$$

In each of the questions and problems below, rather than just drawing a box around your answer, write a sentence or two describing how you solved the problem, the assumptions you made, the reasonableness of your answer, what you learned, and any other facts that you want to include. You may wish to refer to W. Strunk and E. B. White, *The Elements of Style* (New York: Macmillan, 1979) and Joseph M. Williams, *Style: Ten Lessons in Clarity & Grace* (Glenview, Ill.: Scott, Foresman, 1989) to enhance the quality of your sentences. See the Preface for additional generic parts (x), (y), (z) to the home problems.



- P8-1A** Read over the problems at the end of this chapter. Make up an original problem that uses the concepts presented in this chapter. To obtain a solution:

- Make up your data and reaction.
- Use a real reaction and real data. See Problem P4-1 for guidelines.
- Prepare a list of safety considerations for designing and operating chemical reactors. (See <http://www.siri.org/graphics>) See R. M. Felder, *Chem. Eng. Educ.*, 19(4), 176 (1985). The August 1985 issue of *Chemical Engineering Progress* may be useful for part (c).

Load the following POLYMATH/MATLAB programs from the CD-ROM:

P8-2A What if...

- you were asked to prepare a list of safety considerations of redesigning and operating a chemical reactor, what would be the first four items on your list?
- you were asked to give an everyday example that demonstrates the principles discussed in this chapter? (Would sipping a teaspoon of Tabasco or other hot sauce be one?)
- the isomerization of butane reaction (Example 8-6) were carried out adiabatically in a 1.0-m³ pressurized CSTR. What inlet temperature would you recommend between 300 and 600 K?
- you could vary the entering temperature between 300 and 600 K for the butane isomerization in Example 8-6. What inlet temperature would you recommend? Plot the exit conversion as a function of the entering mole fraction of isopentane, keeping the total molar feed rate constant. Describe what you find in each case, noting any maximum in conversion.
- you reconsider production of acetic anhydride in Example 8-7. For the adiabatic case, consider feeding nitrogen ($C_{pN} = 6.25 + 8.78 \times 10^{-3}T - 2.1 \times 10^{-5}T^2$) along with acetone. Plot the conversion as a function of the mole fraction of nitrogen for the same total molar feed rate. Explain why your curve looks the way it does.
- you reconsider Example 8-5 and then make a plot exit conversion as a function of F_{A0} . What would happen if the heat-exchange area were reduced to 4 ft² and the entering temperature decreased to 531°R?
- for nonadiabatic operation of the acetone cracking in Example 8-7, for the same reactor volume, you made plots of the exit conversion and the temperature profiles as a function of reactor diameter, D (recall that



$a = 4/D$). Do you think there is a point at which some of the assumptions in your equations break down?

- (h) you kept the total catalyst weight constant but varied the catalyst particle size in Example 8-10. At what entering temperature does pressure drop have a significant effect on the exit conversion?
- (i) you were able to increase Ua in Example 8-11 by a factor of 5 or 10? What would be the effect on the selectivity S_{BC} ?
- (j) you were able to vary T_a between 0 and 200°C in Example 8-12. What would a plot of the reactor temperature versus T_a look like? (Hint: Compare with Figure 8-24.)
- (k) you were to apply the runaway criteria [Equation (8-77)] to the CSTR in which the butane isomerization (Example 8-6) was taking place? At what inlet temperature would it run away? Under what condition would the SO_2 oxidation run away if it were not safe to exceed a reaction temperature of 1400°C?

P8-3c

The following is an excerpt from *The Morning News*, Wilmington, Delaware (August 3, 1977): "Investigators sift through the debris from blast in quest for the cause [that destroyed the new nitrous oxide plant]. A company spokesman said it appears more likely that the [fatal] blast was caused by another gas—ammonium nitrate—used to produce nitrous oxide." An 83% (wt) ammonium nitrate and 17% water solution is fed at 200°F to the CSTR operated at a temperature of about 510°F. Molten ammonium nitrate decomposes directly to produce gaseous nitrous oxide and steam. It is believed that pressure fluctuations were observed in the system and as a result the molten ammonium nitrate feed to the reactor may have been shut off approximately 4 min prior to the explosion. (a) Can you explain the cause of the blast? [Hint: See P9-3 page 574 and Equation (8-77).] (b) If the feed rate to the reactor just before shutoff was 310 lb of solution per hour, what was the exact temperature in the reactor just prior to shutdown? (c) How would you start up or shut down and control such a reaction? (d) What do you learn when you apply the runaway reaction criteria?

Assume that at the time the feed to the CSTR stopped, there was 500 lb of ammonium nitrate in the reactor. The conversion in the reactor is virtually complete at about 99.99%.

Additional information (approximate but close to the real case):

$$\Delta H_{Rx}^\circ = -336 \text{ Btu/lb ammonium nitrate at } 500^\circ\text{F (constant)}$$

$$C_p = 0.38 \text{ Btu/lb ammonium nitrate} \cdot ^\circ\text{F}$$

$$C_p = 0.47 \text{ Btu/lb of steam} \cdot ^\circ\text{F}$$

$$-r_A V = k C_A V = k \frac{M}{V} V = k M (\text{lb/h})$$

where M is the mass of ammonium nitrate in the CSTR (lb) and k is given by the relationship below.

T (°F)	510	560
k (h ⁻¹)	0.307	2.912

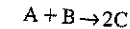
The enthalpies of water and steam are

$$H_1(200^\circ\text{F}) = 168 \text{ Btu/lb}$$

$$H_8(500^\circ\text{F}) = 1202 \text{ Btu/lb}$$



- (e) Explore this problem and describe what you find. (For example, can you plot a form of $R(T)$ versus $G(T)$?) (f) Discuss what you believe to be the point of the problem. The idea for this problem originated from an article by Ben Horowitz. The endothermic liquid-phase elementary reaction



proceeds, substantially, to completion in a single steam-jacketed, continuous-stirred reactor (Table P8-4). From the following data, calculate the steady-state reactor temperature:

Reactor volume: 125 gal
 Steam jacket area: 10 ft²
 Jacket steam: 150 psig (365.9°F saturation temperature)
 Overall heat-transfer coefficient of jacket, U : 150 Btu/h · ft² · °F
 Agitator shaft horsepower: 25 hp
 Heat of reaction, $\Delta H_{Rx}^\circ = +20,000$ Btu/lb mol of A (independent of temperature)

TABLE P8-4

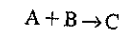
	Component		
	A	B	C
Feed (mol/h)	10.0	10.0	0
Feed temperature (°F)	80	80	—
Specific heat (Btu/lb mol · °F)	51.0	44.0	47.5
Molecular weight	128	94	—
Density (lb/ft ³)	63.0	67.2	65.0

*Independent of temperature.

(Ans: $T = 199^\circ\text{F}$)

(Courtesy of the California Board of Registration for Professional & Land Surveyors.)

- P8-5A The elementary irreversible organic liquid-phase reaction



is carried out adiabatically in a flow reactor. An equal molar feed in A and B enters at 27°C, and the volumetric flow rate is 2 dm³/s.

- (a) Calculate the PFR and CSTR volumes necessary to achieve 85% conversion.
- (b) What is the maximum inlet temperature one could have so that the boiling point of the liquid (550 K) would not be exceeded even for complete conversion?
- (c) Plot the conversion and temperature as a function of PFR volume (i.e., distance down the reactor).
- (d) Calculate the conversion that can be achieved in one 500-dm³ CSTR and in two 250-dm³ CSTRs in series.
- (e) Vary the activation energy $1000 < E < 30,000$ (cal/mol) and heat of reaction $2000 < |\Delta H_{Rx}| < 25,000$ (cal/mol) to learn their effect on the PFR conversion profile.
- (f) Discuss the application of the runaway reaction criteria. What value of T_c would you use to prevent runaway if $\kappa = 3$ at $T_a = 300$ K?

- (g) What do you believe to be the point of this problem?
 (h) Ask another question or suggest another calculation for this reaction.

Additional information:

$$H_A^\circ(273) = -20 \text{ kcal/mol}$$

$$H_B^\circ(273) = -15 \text{ kcal/mol}$$

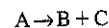
$$H_C^\circ(273) = -41 \text{ kcal/mol}$$

$$C_{A0} = 0.1 \text{ kmol/m}^3$$

$$C_{pA} = C_{pB} = 15 \text{ cal/mol} \cdot \text{K} \quad C_{pC} = 30 \text{ cal/mol} \cdot \text{K}$$

$$k = 0.01 \frac{\text{dm}^3}{\text{mol} \cdot \text{s}} \text{ at } 300 \text{ K} \quad E = 10,000 \text{ cal/mol}$$

P8-6A The elementary irreversible gas-phase reaction



is carried out adiabatically in a PFR packed with a catalyst. Pure A enters the reactor at a volumetric flow rate of $20 \text{ dm}^3/\text{s}$ at a pressure of 10 atm and a temperature of 450 K.

- (a) Plot the conversion and temperature down the plug-flow reactor until an 80% conversion (if possible) is reached. (The maximum catalyst weight that can be packed into the PFR is 50 kg.) Assume that $\Delta P = 0.0$.
 (b) What catalyst weight is necessary to achieve 80% conversion in a CSTR?
 (c) What do you believe to be the point of this problem?

Additional information:

$$C_{pA} = 40 \text{ J/mol} \cdot \text{K} \quad C_{pB} = 25 \text{ J/mol} \cdot \text{K} \quad C_{pC} = 15 \text{ J/mol} \cdot \text{K}$$

$$H_A^\circ = -70 \text{ kJ/mol} \quad H_B^\circ = -50 \text{ kJ/mol} \quad H_C^\circ = -40 \text{ kJ/mol}$$

All heats of formation are referenced to 273 K.

$$k = 0.133 \exp \left[\frac{E}{R} \left(\frac{1}{450} - \frac{1}{T} \right) \right] \frac{\text{dm}^3}{\text{kg} \cdot \text{cat} \cdot \text{s}} \text{ with } E = 31.4 \text{ kJ/mol}$$

P8-7B Repeat Problem P8-6 by taking pressure drop into account in the PFR. The pressure-drop coefficient is

$$\frac{dP}{dW} = -\frac{\alpha}{2} \left(\frac{T}{T_0} \right) \frac{P_0}{(P/P_0)} (1 + \varepsilon X)$$

The reactor can be packed with one of two particle sizes. Choose one.

$$\alpha = 0.019/\text{kg cat. for particle diameter } D_1$$

$$\alpha = 0.0075/\text{kg cat. for particle diameter } D_2$$

- (a) Plot the temperature, conversion, and pressure along the length of the reactor.
 (b) Vary the parameters α and P_0 to learn the ranges of values in which they dramatically affect the conversion.

P8-8B Rework Problem P8-6 for the case when heat is removed by a heat exchanger jacketing the reactor. The flow rate of coolant through the jacket is sufficiently high that the ambient exchanger temperature is constant at 50°C .
 (a) For the PBR:

$$\frac{UA}{\rho_b} = 0.8 \frac{\text{J}}{\text{s} \cdot \text{kg cat.} \cdot \text{K}}$$

where

$$\rho_b = \text{bulk density of the catalyst (kg/m}^3\text{)}$$

$$a = \text{heat-exchange area per unit volume of reactor (m}^2\text{/m}^3\text{)}$$

$$U = \text{overall heat-transfer coefficient (J/s} \cdot \text{m}^2 \cdot \text{K)}$$

What if UA/ρ_b were increased by a factor of 25?

- (b) Make an estimate of the minimum entering temperature at which the reaction will "ignite" (i.e., achieve a reasonable conversion for a reasonable amount of catalyst).
 (c) Find X and T for a "fluidized" CSTR with 80 kg of catalyst.

$$UA = 500 \frac{\text{J}}{\text{s} \cdot \text{K}}, \quad \rho_b = 1 \text{ kg/m}^3$$

- (d) Repeat part (a) for $W = 80.0 \text{ kg}$ assuming a reversible reaction with a reverse specific reaction rate of

$$k_r = 0.2 \exp \left[\frac{E_r}{R} \left(\frac{1}{450} - \frac{1}{T} \right) \right] \left(\frac{\text{dm}^6}{\text{kg cat.} \cdot \text{mol} \cdot \text{s}} \right); \quad E_r = 51.4 \text{ kJ/mol}$$

- (e) Carry out a series of computer experiments in which you vary (UA/ρ_b) between values of 0.1 and 20 ($\text{J/s} \cdot \text{kg cat.} \cdot \text{K}$). In addition, study the effect of ambient temperatures (northern winter-summer operation) on your results. Write a paragraph describing your findings.
 (f) What problems might you encounter if you were to include pressure drop (cf. Problem P8-7)?
 (g) Use or modify the data in this problem to suggest another question or calculation.

P8-9B The formation of styrene from vinylacetylene is essentially irreversible and follows an elementary rate law:



- (a) Determine the conversion achieved in a 10-dm^3 PFR for an entering temperature of 675 K . Plot the temperature and conversion down the length (volume) of the reactor.
 (b) Vary the entering temperature and plot the conversion as a function of entering temperature.
 (c) Vary the ambient temperature in the heat exchanger and find the maximum ambient temperature at which runaway will not occur in the reactor.
 (d) Compare your answers with the case when the reaction is carried out adiabatically.
 (e) Repeat part (b) assuming that the reaction is reversible, $K_C = 100,000$ at 675 K . In addition, a stream of inerts ($C_{p_i} = 100 \text{ J/mol} \cdot ^\circ\text{C}$) with $F_1 =$

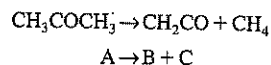
- 3F_{A0} enters the reactor. Plot the conversion as a function of the entering temperature. Is there a maximum? If so, why? If not, why not?
- (f) Ask another question or suggest another calculation that can be made for this problem.

Additional information:

$$\begin{aligned} C_{A0} &= 1 \text{ mol/dm}^3 & Ua &= 5.0 \text{ kJ/s} \cdot \text{dm}^3/\text{K} \\ F_{A0} &= 5 \text{ mol/s} & T_a &= 700 \text{ K} \\ \Delta H_{Rx} &= -231 - 0.012(T - 298) \text{ kJ/mol} \\ C_{pA} &= 0.1222 \text{ kJ/mol} \cdot \text{K} \\ k &= 1.48 \times 10^{11} \exp(-19,124/T) \text{ dm}^3/\text{mol} \cdot \text{s} \\ T_0 &= 675 \text{ K} \end{aligned}$$

[Lundgard, *Int. J. Chem Kinet.*, 16, 125 (1984).]

- P8-10_b** The irreversible endothermic vapor-phase reaction follows an elementary rate law:



and is carried out adiabatically in a 500-dm³ PFR. Species A is fed to the reactor at a rate of 10 mol/min and a pressure of 2 atm. An inert stream is also fed to the reactor at 2 atm. The entrance temperature of both streams is 1100 K.

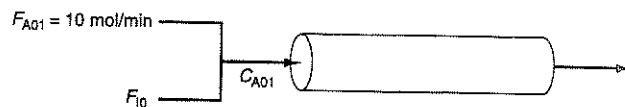


Figure P8-10

- (a) First derive an expression for C_{A01} as a function of C_{A0} and Θ_i .
 (b) Plot the exit conversion as a function of Θ_i .
 (c) Is there a ratio of inerts to the entering molar flow rate of A (i.e., $\Theta_i = F_{I0}/F_{A0}$) at which the conversion is at a maximum? Explain why there "is" or "is not" a maximum.
 (d) How would your answer change if the entering temperature were increased or decreased by 200 K?
 (e) What do you believe to be the point of this problem?

Additional information:

$$\begin{aligned} k &= \exp(34,34 - 34,222/T) \text{ dm}^3/\text{mol} \cdot \text{min} & C_{pI} &= 200 \text{ J/mol} \cdot \text{K} \\ (T \text{ in degrees Kelvin}) \\ C_{pA} &= 170 \text{ J/mol} \cdot \text{K} & C_{pB} &= 90 \text{ J/mol} \cdot \text{K} \\ C_{pC} &= 80 \text{ J/mol} \cdot \text{K} & \Delta H_{Rx} &= 80,000 \text{ J/mol} \end{aligned}$$

- P8-11_c** Derive the energy balance for a packed bed membrane reactor. Apply the balance to the reaction in Problem P8-6 for the case when it is reversible as described in Problem P8-8(d). Species C diffuses out of the membrane.
- (a) Plot the concentration profiles or different values of k_c when the reaction is carried out adiabatically.
- (b) Repeat part (a) when the heat transfer coefficient is the same as that given in P8-8(a). All other conditions are the same as those in Problem P8-6.
- P8-12_b** The elementary irreversible *exothermic* gas phase reaction



is carried out in a packed bed reactor. There is pressure drop in the reactor and the pressure-drop coefficient [(see Equation 4-32)] is 0.007 kg⁻¹. Pure A enters the reactor at a flow rate of 5 mol/s, at a concentration of 0.25 mol/dm³, a temperature of 450 K, and a pressure of 9.22 atm. Heat is removed by a heat exchanger jacketing the reactor. The coolant flow rate in the jacket is sufficient to maintain the ambient temperature of the heat exchanger at 27°C. The term giving the product of the heat-transfer coefficient and area per unit volume divided by the bulk catalyst density is

$$\frac{Ua}{\rho_b} = \frac{5 \text{ J}}{\text{kg cat.} \cdot \text{s} \cdot \text{K}}$$

where

ρ_b = bulk density of catalyst (kg/m³)

a = heat-exchange area per unit volume of reactor (m²/m³)

U = overall heat-transfer coefficient $\left(\frac{\text{J}}{\text{m}^2 \cdot \text{s} \cdot \text{K}} \right)$

The maximum weight of catalyst that can be packed in this reactor is 50 kg.

- (a) Plot the temperature, conversion X , and the pressure ratio ($y = P/P_0$) as a function of catalyst weight.
 (b) At what catalyst weight down the reactor does the rate of reaction ($-r'_A$) reach its maximum value?
 (c) At what catalyst weight down the reactor does the temperature reach its maximum value?
 (d) What happens when the heat-transfer coefficient is doubled? What happens if the heat coefficient is halved? Discuss your observations on the effects on reactor performance (i.e., conversion, temperature, and pressure drop).

Additional information:

$$\Delta H_{Rx} = -20,000 \text{ J/mol A at } 273 \text{ K}$$

$$C_{pA} = 40 \text{ J/mol} \cdot \text{K} \quad C_{pB} = 20 \text{ J/mol} \cdot \text{K}$$

$$k = \exp \left[\frac{E}{R} \left(\frac{1}{450} - \frac{1}{T} \right) \right] \frac{\text{dm}^3}{\text{kg} \cdot \text{cat.} \cdot \text{s}}$$

with

$$E = 31.4 \frac{\text{kJ}}{\text{mol}} \quad R = 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$

$$\text{Hence } E/R = 3776.76 \text{ K.}$$

P8-13_A The adiabatic equilibrium conversion for the reaction



is carried out in a series of staged packed-bed reactors with interstage cooling. The lowest temperature to which the reactant stream may be cooled is 27°C. The feed is equal molar in A and B and the catalyst weight in each reactor is sufficient to achieve 99.9% of the equilibrium conversion. The feed enters at 27°C and the reaction is carried out adiabatically. If four reactors and three coolers are available, what conversion may be achieved?

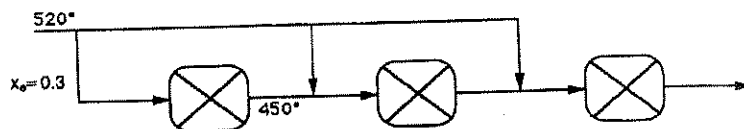
Additional information:

$$\Delta H_{R_{25}} = -30,000 \text{ cal/mol A} \quad C_{p_A} = C_{p_B} = C_{p_C} = C_{p_D} = 25 \text{ cal/g mol} \cdot \text{K}$$

$$K_e(50^\circ\text{C}) = 500,000 \quad F_{A0} = 10 \text{ mol A/min}$$

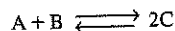
First prepare a plot of equilibrium conversion as a function of temperature. [Partial ans.: $T = 360 \text{ K}$, $X_e = 0.984$; $T = 520 \text{ K}$, $X_e = 0.09$; $T = 540 \text{ K}$, $X_e = 0.057$]

P8-14_A Figure 8-8 shows the temperature-conversion trajectory for a train of reactors with interstage heating. Now consider replacing the interstage heating with injection of the feed stream in three equal portions as shown below:



Sketch the temperature-conversion trajectories for (a) an endothermic reaction with entering temperatures as shown, and (b) an exothermic reaction with the temperatures to and from the first reactor reversed.

P8-15_B The elementary reversible gas-phase reaction



is to be carried out in a PFR and a CSTR. The feed contains only A and B in stoichiometric proportions at 580.5 kPa and 77°C. The molar feed rate of A is 20 mol/s. The reaction is carried out adiabatically.

- Determine the plug-flow reactor volume necessary to achieve 85% of the adiabatic equilibrium conversion.
- Plot $-r_A$, X , and T as a function of reactor length if the cross-sectional area is 0.01 m^2 . What do the plots suggest about changing the feed conditions?
- Determine the conversion that can be achieved in a 1.5-m^3 CSTR with a heat exchanger mounted inside.
- Repeat parts (a) and (c) for the case of an endothermic reaction with a $\Delta H_{R_{25}}$ of the same absolute magnitude but with an entering temperature of 277°C.
- Comment on the magnitudes of $\Delta H_{R_{25}}$, E , K_C , and U . When (or under what conditions) might "runaway" occur?
- Use a software package to study the effect of the ambient temperature T_a (winter-summer) on part (c).

Additional information:

Rate-law parameters:

$$k = 0.035 \text{ dm}^3/\text{mol} \cdot \text{min at } 273 \text{ K}$$

$$E = 70,000 \text{ J/mol}$$

Thermodynamic parameters at 25°C:

$$H_A^\circ = -40 \text{ kJ/mol} \quad C_{p_A} = 25 \text{ J/mol} \cdot \text{K}$$

$$H_B^\circ = -30 \text{ kJ/mol} \quad C_{p_B} = 15 \text{ J/mol} \cdot \text{K}$$

$$H_C^\circ = -45 \text{ kJ/mol} \quad C_{p_C} = 20 \text{ J/mol} \cdot \text{K}$$

$$K_C = 25,000$$

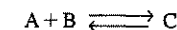
Heat-exchanger data:

$$\text{Overall heat-transfer coefficient} = 10 \text{ W/m}^2 \cdot \text{K}$$

$$\text{Exchanger area} = 2 \text{ m}^2$$

$$\text{Ambient temperature} = 17^\circ\text{C}$$

P8-16_B The elementary liquid-phase reaction



is to be carried out adiabatically in a set of tubular reactors packed with a resin catalyst and arranged in series. The feed consists of 25 mol % A, 25 mol % B, and 50 mol % inerts at 300 K. There are available to you a large number of interstage heat exchangers that can cool the reaction stream to temperatures as low as 300 K. The reactors have sufficient catalyst to reach 95% of the corresponding equilibrium conversion. What is the smallest number of reactors in series necessary to obtain an exiting conversion above 50%? What would you need to do to increase the conversion to 95%? What concerns would you have about reaching 95% conversion?

Additional information:

$$C_{p_A} = 2.0 \text{ cal/g mol} \cdot ^\circ\text{C} \quad C_{p_C} = 7.0 \text{ cal/g mol} \cdot ^\circ\text{C}$$

$$C_{p_B} = 5.0 \text{ cal/g mol} \cdot ^\circ\text{C} \quad C_{p_I} = 1.5 \text{ cal/g mol} \cdot ^\circ\text{C}$$

$$\Delta H_{R_{25}}^\circ(273 \text{ K}) = -10,000 \text{ cal/g mol A}$$

$$F_{A0} = 10 \text{ mol/min}$$

$T \text{ (K)}$	350	400	450	500	550	600	650	700
X_e	1.00	0.97	0.74	0.4	0.2	0.1	0.06	0.04

P8-17_B The first-order irreversible exothermic liquid-phase reaction



is to be carried out in a jacketed CSTR. Species A and an inert I are fed to the reactor in equimolar amounts. The molar feed rate of A is 80 mol/min.

- What is the reactor temperature for a feed temperature of 450 K?

- (b) Plot the reactor temperature as a function of the feed temperature.
 (c) To what inlet temperature must the fluid be preheated for the reactor to operate at a high conversion? What are the corresponding temperature and conversion of the fluid in the CSTR at this inlet temperature?
 (d) Suppose that the fluid is now heated 5°C above the temperature in part (c) and then cooled 20°C, where it remains. What will be the conversion?
 (e) What is the inlet extinction temperature for this reaction system? (Ans.: $T_0 = 87^\circ\text{C}$.)

Additional information:

Heat capacity of the inert: $30 \text{ cal/g mol} \cdot ^\circ\text{C}$

Heat capacity of A and B: $20 \text{ cal/g mol} \cdot ^\circ\text{C}$

UA : $8000 \text{ cal/min} \cdot ^\circ\text{C}$

Ambient temperature, T_a : 300 K

$\tau = 100 \text{ min}$

$\Delta H_{Rx} = -7500 \text{ cal/mol}$

$k = 6.6 \times 10^{-3} \text{ min}^{-1}$ at 350 K

$E = 40,000 \text{ cal/mol} \cdot \text{K}$

- P8-18_A** Radial flow reactors are used to help eliminate hot spots in highly exothermic reactions. The velocity is highest at the inlet and then decreases as $1/r$ as the fluid moves away from the inlet. The overall heat-transfer coefficient varies with the square root of the radial velocity:

$$U = U(r=r_0) \left(\frac{\text{velocity at } r_0}{\text{velocity at } r} \right)^{1/2}$$

and at the inlet $U = U(r=r_0) = 100 \text{ Btu/h} \cdot \text{ft}^2 \cdot ^\circ\text{F}$.

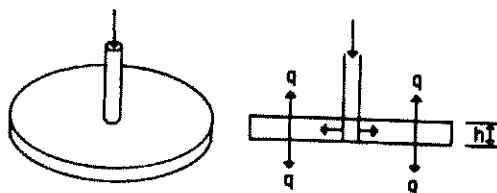


Figure P8-18 Radial flow reactor.

- (a) Rework Problem P8-6 for a radial reactor.
 (b) Rework Problem P8-12 for a radial reactor.
 (c) Consider the flow conditions to one of the tubes for the SO_2 oxidation described in Example 8-10. Replace the tube with a radial flow reactor 1 cm in height with an inlet diameter of 0.5 cm. The reactor is immersed in the same boiling liquid as in Example 8-10. Plot the temperature and conversion as a function of radius and catalyst weight for three different inlet temperatures. Study the behavior of this reactor by varying a number of parameters, such as flow rate and gas composition.

- (d) The reaction discussed in Problem P8-15 is to be carried out in a single plug-flow reactor immersed in a coolant and in a radial flow reactor immersed in the same coolant. The tubular flow reactor is 2 ft in diameter. The height of the radial flow reactor is $\frac{1}{2}$ in. and the diameter of the inlet is 1 in. In both cases the coolant temperature is 100°C and the overall heat-transfer coefficient is $2000 \text{ J/m}^2 \cdot \text{h} \cdot ^\circ\text{C}$. Plot conversion and temperatures as a function of reactor radius.

P8-19_C The zero-order exothermic liquid-phase reaction



is carried out at 85°C in a jacketed 0.2-m^3 CSTR. The coolant temperature in the reactor is 32°F . The heat transfer coefficient is $120 \text{ W/m}^2 \cdot \text{K}$. Determine the critical value of the heat-transfer area below which the reactor will run away and explode [Chem. Eng., 91(10), 54 (1984)].

Additional information:

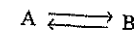
Specific reaction rate:

$$k = 1.127 \text{ kmol/m}^3 \cdot \text{min at } 40^\circ\text{C}$$

$$k = 1.421 \text{ kmol/m}^3 \cdot \text{min at } 50^\circ\text{C}$$

The heat capacity of the solution is 4 J/g . The solution density is 0.90 kg/dm^3 . The heat of reaction is -500 J/g . The feed temperature is 40°C and the feed rate is 90 kg/min . MW of A = 90 g/mol .

P8-20_B The elementary reversible liquid-phase reaction



takes place in a CSTR with a heat exchanger. Pure A enters the reactor.

- (a) Derive an expression (or set of expressions) to calculate $G(T)$ as a function of heat of reaction, equilibrium constant, temperature, and so on. Show a sample calculation for $G(T)$ at $T = 400 \text{ K}$.
 (b) What are the steady-state temperatures? (Ans.: 310, 377, 418 K)
 (c) Which steady states are locally stable?
 (d) What is the conversion corresponding to the upper steady state?
 (e) Vary the ambient temperature T_a and make a plot of the reactor temperature as a function of T_a , identifying the ignition and extinction temperatures.
 (f) If the heat exchanger in the reactor suddenly fails (i.e., $UA = 0$), what would be the conversion and the reactor temperature when the new upper steady state is reached? (Ans.: 431 K)
 (g) What is the adiabatic blow out flow rate, v_0 .
 (h) Suppose that you want to operate at the lower steady state. What parameter values would you suggest to prevent runaway?

Additional information:

$$UA = 3600 \text{ cal/min} \cdot \text{K}$$

$$E/R = 20,000 \text{ K}$$

$$C_{pA} = C_{pB} = 40 \text{ cal/mol} \cdot \text{K}$$

$$V = 10 \text{ dm}^3$$

$$\Delta H_{Rx} = -80,000 \text{ cal/mol A}$$

$$v_0 = 1 \text{ dm}^3/\text{min}$$

$$K_{eq} = 100 \text{ at } 400 \text{ K}$$

$$F_{A0} = 10 \text{ mol/min}$$

$$k = 1 \text{ min}^{-1} \text{ at } 400 \text{ K}$$

$$\text{Ambient temperature, } T_a = 37^\circ\text{C}$$

$$\text{Feed temperature, } T_0 = 37^\circ\text{C}$$

P8-21_C The first-order irreversible liquid-phase reaction

is to be carried out in a jacketed CSTR. Pure A is fed to the reactor at a rate of 0.5 g mol/min. The heat-generation curve for this reaction and reactor system,

$$G(T) = \frac{-\Delta H_{Rx}^0}{1 + 1/\tau K}$$

is shown in Figure P8-21.

- To what inlet temperature must the fluid be preheated for the reactor to operate at a high conversion? (Ans.: $T_0 \geq 214^\circ\text{C}$.)
- What is the corresponding temperature of the fluid in the CSTR at this inlet temperature? (Ans.: $T_s = 164^\circ\text{C}$, 184°C .)
- Suppose that the fluid is now heated 5°C above the temperature in part (a) and then cooled 10°C , where it remains. What will be the conversion? (Ans.: $X = 0.9$.)
- What is the extinction temperature for this reaction system? (Ans.: $T_0 = 200^\circ\text{C}$.)

Additional information:

Heat of reaction (constant): -100 cal/g mol A

Heat capacity of A and B: 2 cal/g mol $\cdot^\circ\text{C}$

UA : 1 cal/min $\cdot^\circ\text{C}$

Ambient temperature, T_a : 100°C

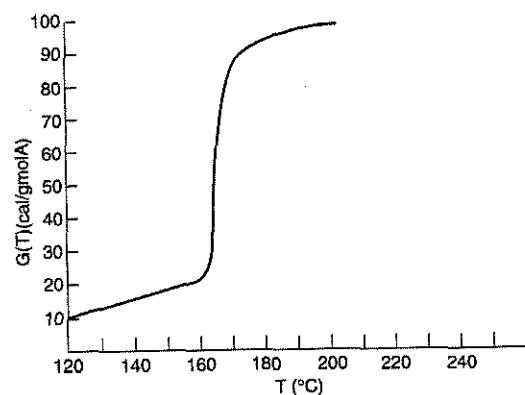
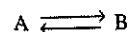


Figure P8-21 $G(T)$ curve.

P8-22_A The reversible elementary reaction

is carried out in a CSTR. Plot the heat-generated and heat-removed curves on the same graph.

- How many multiple steady states are there?
- What is the effect of changing air temperatures, T_a (winter-summer) on multiple steady states?

Additional information:

$$\Delta H_{Rx}^0 = -80 \text{ kJ/mol A} \quad F_{A0} = 10 \text{ mol/s} \quad C_{A0} = 2 \text{ mol/dm}^3$$

$$UA = 2000 \frac{\text{J}}{\text{K} \cdot \text{s}}$$

$$V = 500 \text{ dm}^3$$

$$T_a = 40^\circ\text{C}$$

$$k = 0.001 \text{ s}^{-1} \text{ at } 373 \text{ K}$$

$$C_{pA} = C_{pB} = 40 \text{ J/mol} \cdot \text{K}$$

$$E = 150 \text{ kJ/mol}$$

$$K_e = 100 \text{ at } 350 \text{ K}$$

$$T_0 = 27^\circ\text{C}$$

- Make a plot of the reactor temperature T as a function of inlet temperature T_0 . What are the ignition and extinction temperatures?
- Repeat parts (a), (b), and (c) for the case when the reaction is irreversible with $K_e = \infty$.

P8-23_B The vapor-phase cracking of acetone is to be carried out adiabatically in a bank of 1000 1-in. schedule 40 tubes 10 m in length. The molar feed rate of acetone is 6000 kg/h at a pressure of 500 kPa. The maximum feed temperature is 1050 K. Nitrogen is to be fed together with the acetone to provide the sensible heat of reaction. Determine the conversion as a function of nitrogen feed rate (in terms of Θ_{N_2}) for

- Fixed total molar flow rate.
- Molar flow rate increasing with increasing Θ_{N_2} .

P8-24_C This chapter neglected radial variations in temperature and concentration.

- Use a shell balance on the segment shown in Figure P8-24a to arrive at the steady energy and mole balances that account for axial variations in concentration and both radial and axial variations in temperature.

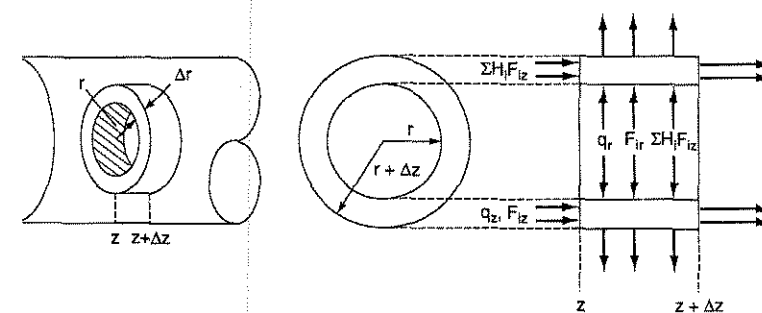


Figure P8-24a Shell balance.

Show that

$$-\frac{\partial q_z}{\partial z} - \frac{1}{r} \frac{\partial(rq_r)}{\partial r} - \sum_{i=1}^m u C_i C_{pi} \frac{\partial T}{\partial z} + r_A \Delta H_{Rx} = 0 \quad (\text{P8-24.1})$$

where u is the superficial velocity (m/s) and q is the heat flux ($\text{J/m}^2 \cdot \text{s}$).

- (b) Let k_e be the effective thermal conductivity in both the axial and radial directions and use Fourier's law,

$$q_z = -k_e \frac{\partial T}{\partial z} \quad \text{and} \quad q_r = -k_e \frac{\partial T}{\partial r}$$

to show that

$$k_e \frac{\partial^2 T}{\partial z^2} + k_e \frac{\partial^2 T}{\partial r^2} + \frac{k_e}{r} \frac{\partial T}{\partial r} - u \sum_{i=1}^m C_i C_{pi} \frac{\partial T}{\partial z} + r_A(C_i, T) \Delta H_{Rx} = 0 \quad (\text{P8-24.2})$$

- (c) Explain the use of the following boundary conditions:

$$\text{At } r = R, \text{ then } U(T_R(z) - T_a) = -k_e \frac{\partial T}{\partial r} \quad (\text{P8-24.3})$$

$$\text{At } r = 0, \text{ then } \frac{\partial T}{\partial r} = 0 \quad (\text{P8-24.4})$$

- (d) At the entrance and exit of the reactor, there are different boundary conditions that can be used depending on the degree of sophistication required. Explain why the simplest (see Chapter 14) set is

$$\text{At } z = 0, \quad T = T_0 \quad \text{and} \quad C_i = C_{i0} \quad (\text{P8-24.5})$$

$$\text{At } z = L, \quad \frac{\partial T}{\partial z} = 0 \quad \text{and} \quad \frac{\partial C_i}{\partial z} = 0 \quad (\text{P8-24.6})$$

One can usually neglect conduction in the axial directions with respect to convection.

- (e) Sketch the radial temperature gradients down a PFR for
- (1) An exothermic reaction.
 - (2) An endothermic reaction.
 - (3) An exothermic reaction carried out adiabatically.
- (f) Use the data in Problem P8-7 to account for radial temperature gradients in the reactor.

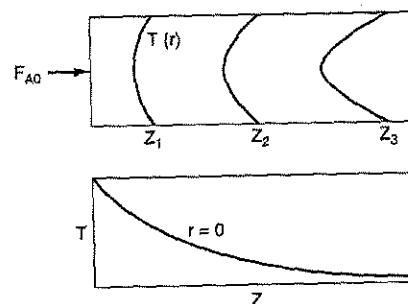


Figure P8-24b Endothermic reaction profiles.

Additional information:

$$k_e = 0.4 \frac{\text{cal}}{\text{cm} \cdot \text{min} \cdot \text{K}}$$

Reactor diameter = 3 cm

Plot temperature reaction rate as a function of radius at specific locations down the reactor. Plot the centerline temperature as a function of conversion.

- (g) What do you think about neglecting radial variations in concentration? Read Chapter 11, then show that

$$k_e \frac{\partial^2 T}{\partial z^2} + k_e \frac{\partial^2 T}{\partial r^2} + \frac{k_e}{r} \frac{\partial T}{\partial r} - u \sum_{j=1}^m C_j C_{pj} \frac{\partial T}{\partial z} + \left(\sum_{j=1}^m C_j D_e \frac{\partial C_j}{\partial r} \right) \frac{\partial T}{\partial r} + r_A(C_j, T) \Delta H_{Rx} = 0 \quad (\text{P8-24.7})$$

where D_e is the effective diffusivity. (Experts only)

- P8-25_C A reaction is to be carried out in the packed-bed reactor shown in Figure P8-25.



Figure P8-25

The reactants enter in the annular space between an outer insulated tube and an inner tube containing the catalyst. No reaction takes place in the annular region. Heat transfer between the gas in this packed-bed reactor and the gas flowing counter currently in the annular space occurs along the length of the reactor. The overall heat-transfer coefficient is $5 \text{ W/m}^2 \cdot \text{K}$. Plot the conversion and temperature as a function of reactor length for the data given in

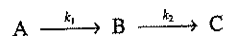
- (a) Problem P8-5.
- (b) Problem P8-6.
- (c) Problem P8-15.

- P8-26_B (Position of reaction front) Using the computer program (or a slight variation thereof) given in Example 8-10, determine the effect on the temperature and conversion profiles of varying the inlet temperature when the reaction is carried out adiabatically. In particular, study the effect of the inlet temperature on the position of the reaction front (i.e., the position where the temperature rises very steeply).

- P8-27_C (Optimum inlet temperature for sulfur dioxide oxidation) Using the same data, feed flow rate, and composition as given in Example 8-10, determine the inlet temperature that will give the maximum conversion of SO_2 in an existing tubular reactor containing 2500 lb of V_2O_5 that is operated adiabatically. (Hint: Only a slight modification of the computer program shown in Section 8.10 may be necessary to find this optimum T_0 .)

- P8-28_B You are an engineer who is to design a CSTR for the elementary consecutive gas-phase reactions

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The feed conditions and desired product specifications are known, together with the temperature of the heating medium. It is your job to design the reactor, that is, to specify the reactor volume and the area of the heating coil inside the reactor.

(a) Calculate the desired operating temperature inside the reactor. (Ans.: 269°F.)

(b) Calculate the volume of the reactor. (Ans.: 6.58 ft³.)

(c) Calculate the area of the heating coil. (Ans.: 18.1 ft².)

(d) Find a set of conditions that will give multiple steady states if reaction 1 is exothermic rather than endothermic. How many steady states can you find? (Ans.: 5.) Make a plot of $G(T)$ vs. $R(T)$ and of T_s vs. T_0 .

Additional information:

Product:

The ratio C_B/C_C is equal to 10.
50% of A in the feed is converted.

Feed:

The feed is gas-phase and pure A.
The molar flow rate is 0.05 lb mol/s.
The volumetric flow rate is 7.85 ft³/s.
The temperature is 400°F.
The pressure in the reactor is 4 atm.

Heat capacities:

C_p 's of A, B, and C are all 25 Btu/lb mol·°F.

Reaction 1:

$$A_1 = 2 \times 10^9 \text{ s}^{-1}$$

$$E_1 = 31,000 \text{ Btu/lb mol}$$

$$\Delta H_{R1} = 15,000 \text{ Btu/lb mol A reacted}$$

Reaction 2:

$$A_2 = 1 \times 10^{11} \text{ s}^{-1}$$

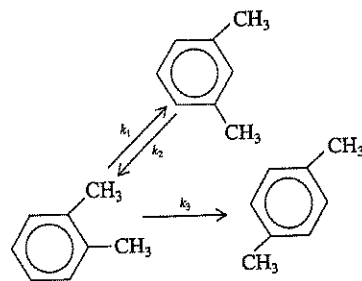
$$E_2 = 40,000 \text{ Btu/lb mol}$$

$$\Delta H_{R2} = -20,000 \text{ Btu/lb mol C reacted}$$

Heat transfer:

The heating medium is saturated high-pressure steam at 350°F.
The overall heat-transfer coefficient between the heating medium and the reaction mixture is 400 Btu/h·ft²·°F.

P8-29c (Multiple reactions with heat effects) Xylene has three major isomers, *m*-xylene, *o*-xylene, and *p*-xylene. When *o*-xylene is passed over a Cryotite catalyst, the following elementary reactions are observed:



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The feed to the reactor is equal molar in both *m*-xylene and *o*-xylene (species A and B). For a total feed rate of 2 mol/min and the reaction conditions below, plot the temperature and the molar flow rates of each species as a function of catalyst weight up to a weight of 100 kg.

- Find the lowest concentration of *o*-xylene achieved in the reactor.
- Find the highest concentration of *m*-xylene achieved in the reactor.
- Find the maximum concentration of *o*-xylene in the reactor.
- Repeat parts (a) to (d) for a pure feed of *o*-xylene.
- Vary some of the system parameters and describe what you learn.
- What do you believe to be the point of this problem?

Additional information:²⁴

All heat capacities are virtually the same at 100 J/mol·K.

$$C_{T0} = 2 \text{ mol/dm}^3$$

$$\Delta H_{R10} = -1800 \text{ J/mol } o\text{-xylene}^{24}$$

$$\Delta H_{R230} = -1100 \text{ J/mol } o\text{-xylene}^{24}$$

$$k_1 = 0.5 \exp[2(1 - 320/T)] \text{ dm}^3/\text{kg cat} \cdot \text{min}$$

$$k_2 = k_1/K_C$$

$$k_3 = 0.005 \exp\{[4.6(1 - (460/T))]\} \text{ dm}^3/\text{kg cat} \cdot \text{min}$$

$$K_C = 10 \exp[4.8(430/T - 1.5)]$$

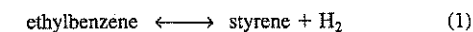
$$T_0 = 330 \text{ K}$$

$$T_a = 500 \text{ K}$$

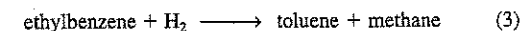
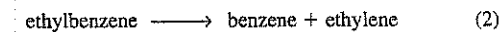
$$Ua/\rho_b = 16 \text{ J/kg cat} \cdot \text{min} \cdot ^\circ\text{C}$$

$$W = 100 \text{ kg}$$

P8-30c (Multiple reactions with heat effects) Styrene can be produced from ethylbenzene by the following reaction:



However, several irreversible side reactions also occur:



[J. Snyder and B. Subramaniam, *Chem. Eng. Sci.*, 49, 5585 (1994)]. Ethylbenzene is fed at a rate of 0.00344 kmol/s to a 10.0-m³ PFR reactor along with inert steam at a total pressure of 2.4 atm. The steam/ethylbenzene molar ratio is initially [i.e., parts (a) to (c)] 14.5:1 but can be varied. Given the following data, find the exiting molar flow rates of styrene, benzene, and toluene for the following inlet temperatures when the reactor is operated adiabatically.

- $T_0 = 800 \text{ K}$
- $T_0 = 930 \text{ K}$
- $T_0 = 1100 \text{ K}$

²⁴ Obtained from inviscid pericosity measurements.



- (d) Find the ideal inlet temperature for the production of styrene for a steam/ethylbenzene ratio of 58:1. (*Hint*: Plot the molar flow rate of styrene versus T_0 . Explain why your curve looks the way it does.)
- (e) Find the ideal steam/ethylbenzene ratio for the production of styrene at 900 K. [*Hint*: See part (d).]
- (f) What do you believe to be the points of this problem?
- (g) Ask another question or suggest another calculation that can be made for this problem.

Additional information:

Heat capacities

Methane	68 J/mol·K	Styrene	273 J/mol·K
Ethylene	90 J/mol·K	Ethylbenzene	299 J/mol·K
Benzene	201 J/mol·K	Hydrogen	30 J/mol·K
Toluene	249 J/mol·K	Steam	40 J/mol·K

$$\rho = 2137 \text{ kg/m}^3 \text{ of pellet}$$

$$\phi = 0.4$$

$$\Delta H_{R1EB} = 118,000 \text{ kJ/kmol ethylbenzene}$$

$$\Delta H_{R2EB} = 105,200 \text{ kJ/kmol ethylbenzene}$$

$$\Delta H_{R3EB} = -53,900 \text{ kJ/kmol ethylbenzene}$$

$$K_{p1} = \exp \left\{ b_1 + \frac{b_2}{T} + b_3 \ln(T) + [(b_4 T + b_5) T + b_6] T \right\} \text{ atm}$$

$$b_1 = -17.34$$

$$b_4 = -2.314 \times 10^{-10}$$

$$b_2 = -1.302 \times 10^4$$

$$b_5 = 1.302 \times 10^{-6}$$

$$b_3 = 5.051$$

$$b_6 = -4.931 \times 10^{-3}$$

The kinetic rate laws for the formation of styrene (St), benzene (B), and toluene (T), respectively, are as follows. ($_{EB}$ = ethylbenzene)

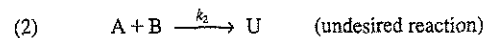
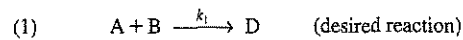
$$r_{1S} = \rho(1 - \phi) \exp \left(-0.08539 - \frac{10,925}{T} \right) \left(P_{EB} - \frac{P_{St} P_{H_2}}{K_{p1}} \right) \text{ (kmol/m}^3 \cdot \text{s)}$$

$$r_{2B} = \rho(1 - \phi) \exp \left(13.2392 - \frac{25,000}{T} \right) (P_{EB}) \text{ (kmol/m}^3 \cdot \text{s)}$$

$$r_{3T} = \rho(1 - \phi) \exp \left(0.2961 - \frac{11,000}{T} \right) (P_{EB} P_{H_2}) \text{ (kmol/m}^3 \cdot \text{s)}$$

The temperature T is in kelvin.

P8-31_B The liquid-phase reactions



are carried out in a perfectly insulated CSTR. The desired reaction is first order in A and zero order in B, while the undesired reaction is zero order in A and first order in B. The feed rate is equimolar in A and B. Species A enters the reactor at a temperature of 100°C and species B enters at a temperature of 50°C. The operating temperature of the reactor is 400 K. The molar flow rate of A entering the reactor is 60 mol/min: $C_{pA} = 20 \text{ cal/mol} \cdot \text{K}$, $C_{pB} = 30 \text{ cal/mol} \cdot \text{K}$, $C_{pD} = 50 \text{ cal/mol} \cdot \text{K}$, and $C_{pU} = 40 \text{ cal/mol} \cdot \text{K}$.

$$\text{For reaction 1: } \Delta H_{R1} = -3000 \text{ cal/mol of A at 300 K}$$

$$\text{For reaction 2: } \Delta H_{R2} = -5000 \text{ cal/mol of A at 300 K}$$

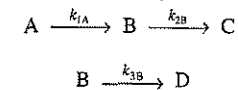
$$k_1 = 1000 \exp \left(-\frac{2000}{T} \right) \text{ min}^{-1} \quad (T \text{ is in kelvin})$$

$$k_2 = 2000 \exp \left(-\frac{3000}{T} \right) \text{ min}^{-1}$$

$$C_{A0} = 0.01 \text{ mol/dm}^3 \quad 0.001 \frac{\text{mol}}{\text{dm}^3} < C_{B0} < 2 \text{ mol/dm}^3$$

- (a) What will be the exit molar flow rates of U and D from the reactor?
- (b) What is the CSTR reactor volume for the conditions specified above?
- (c) Is there a more effective way to maximize D? Explain.
- (*Hint*: Start with a mole balance on A. Outline your method before beginning any calculations.)

P8-32_C The liquid phase reactions



can be carried out in a number of CSTRs. Currently, the following sizes are available, 4 dm³, 40 dm³, 400 dm³, 4000 dm³. You can use up to 4 CSTRs of any one size. The heat flow to each reactor is controlled by adjusting the functional area f ($0 \leq f < 1.0$).

$Q_r = 100 f(T - T_a)$ (cal/min) where the ambient temperature can be varied between 0°C and 100°C.

$$k_{1A} = 0.3 e^{7000 \left(\frac{1}{300} - \frac{1}{T} \right)} \text{ min}^{-1}$$

$$k_{2B} = 0.03 e^{7000 \left(\frac{1}{300} - \frac{1}{T} \right)} \text{ min}^{-1}$$

$$k_{3B} = 0.1 e^{4000 \left(\frac{1}{300} - \frac{1}{T} \right)} \text{ dm}^3/\text{mol} \cdot \text{min}$$

The concentration of pure A is 5 M. A can be diluted with solvent. The feed can be cooled to 0°C or heated to 100°C.

$$\Delta H_{R1A} = +10,000 \text{ cal/mol A}$$

$$\Delta H_{R2B} = -10,000 \text{ cal/mol B}$$

$$\Delta H_{R3B} = -100,000 \text{ cal/mol B}$$

Discuss how should the reaction be carried (i.e. $v_0 =$, $T_0 =$, etc.) out to produce 100 mol B/day? [No ans. given in solutions manual to this revised problem]

JOURNAL CRITIQUE PROBLEMS

- P8C-1** Equation (8) in an article in *J. Chem. Technol. Biotechnol.*, 31, 273 (1981) is the kinetic model of the system proposed by the authors. Starting from Equation (2), derive the equation that describes the system. Does it agree with Equation (8)? By using the data in Figure 1, determine the new reaction order. The data in Table 2 show the effect of temperature. Figure 2 illustrates this effect. Use Equation (8) and Table 2 to obtain Figure 2. Does it agree with the article's results? Now use Table 2 and your equation. How does the figure obtained compare with Figure 2? What is your new E_{ac} ?
- P8C-2** The kinetics of the reaction of sodium hypochlorite and sodium sulfate were studied by the flow thermal method in *Ind. Eng. Chem. Fundam.*, 19, 207 (1980). What is the flow thermal method? Can the energy balance developed in this article be applied to a plug-flow reactor, and if not, what is the proper energy balance? Under what conditions are the author's equations valid?
- P8C-3** In an article on the kinetics of sucrose inversion by invertase with multiple steady states in a CSTR [*Chem. Eng. Commun.*, 6, 151 (1980)], consider the following challenges: Are the equations for K_i and K_m correct? If not, what are the correct equations for these variables? Can an analysis be applied to this system to deduce regions of multiple steady states?
- P8C-4** Review the article in *AIChE J.*, 16, 415 (1970). How was the $G(T)$ curve generated? Is it valid for a CSTR? Should $G(T)$ change when the space time changes? Critique the article in light of these questions.

CD-ROM MATERIAL

• Learning Resources

1. Summary Notes for Lectures 13, 14, 15, 16, 17, and 35A
2. Interactive Computer Modules
 - A. Heat Effects I
 - B. Heat Effects II
3. Solved Problems
 - A. Example CD8-1 $\Delta H_{Rx}(T)$ for Heat Capacities Expressed as Quadratic Functions of Temperature
 - B. Example CD8-2 Second Order Reaction Carried Out Adiabatically in a CSTR
4. PFR/PBR Solution Procedure for a Reversible Gas-Phase Reaction
5. Living Example Problems
 1. Example 8-5 CSTR with a Cooling Coil
 2. Example 8-6 Liquid Phase Isomerization of Normal Butane
 3. Example 8-7 Production of Acetic Anhydride
 4. Example 8-10 Oxidation of SO_2
 5. Example 8-11 Parallel Reaction in a PFR with Heat Effects
 6. Example 8-12 Multiple Reactions in a CSTR



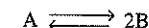
• Professional Reference Shelf

1. Steady State Bifurcation Analysis

- A. Fundamentals
- B. Example CD8-3 Determine the Parameters That Give Multiple Steady States (MSS)

• Additional Homework Problems

CDP8-A_B The exothermic reaction



is carried out in both a plug-flow reactor and a CSTR with heat exchange. You are requested to plot conversion as a function of reactor length for both adiabatic and nonadiabatic operation as well as to size a CSTR. [2nd Ed. P8-16]

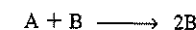
CDP8-B_B Use bifurcation theory (Section 8.6.5 on the CD-ROM) to determine the possible regions for multiple steady states for the gas reaction with the rate law

$$-r_A'' = \frac{k_1 C_A}{(k_2 + k_3 C_A)^2}$$

[2nd Ed. P8-26]

CDP8-C_B In this problem bifurcation theory (CD-ROM Section 8.6.5) is used to determine if multiple steady states are possible for each of three types of catalyst. [2nd Ed. P8-27_B]

CDP8-D_B In this problem bifurcation theory (CD-ROM Section 8.6.5) is used to determine the regions of multiple steady states for the autocatalytic reaction



[2nd Ed. P8-28_B]

CDP8-E_C This problem concerns the SO_2 reaction with heat losses. [2nd Ed. P8-33]

CDP8-F_C This problem concerns the use of interstage cooling in SO_2 oxidation. [2nd Ed. P8-34a]

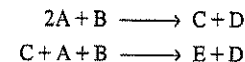
CDP8-G_B This problem is a continuation of the SO_2 oxidation example problem. Reactor costs are considered in the analysis cooling. [2nd Ed. P8-34(b and c)]

CDP8-H_B Parallel reactions take place in a CSTR with heat effects. [1st Ed. P9-21]

CDP8-I_B This problem concerns multiple steady states for the second-order reversible liquid-phase reaction. [Old exam problem]

CDP8-J_B Series reactions take place in a CSTR with heat effects. [1st Ed. P9-23]

CDP8-K_B A drug intermediate is produced in a batch reactor with heat effects. The reaction sequence is



The desired product is C.

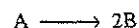
CDP8-L_B In the multiple steady state for



CDP8-M_B The phase plane of C_A vs. T shows a separatrix. [2nd Ed. P8-22]
An acid-catalyzed second-order reaction is carried out adiabatically in a CSTR.

CDP8-N_B A second-order reaction with multiple steady states is carried out in different solvents.

CDP8-O_B Multiple reactions



are carried out adiabatically in a PFR.

CDP8-P_B Exothermic second-order reversible reaction carried out in a packed bed reactor.

SUPPLEMENTARY READING

1. An excellent development of the energy balance is presented in

ARIS, R., *Elementary Chemical Reactor Analysis*. Upper Saddle River, N.J.: Prentice Hall, 1969, Chaps. 3 and 6.

HIMMELBLAU, D. M., *Basic Principles and Calculations in Chemical Engineering*, 4th ed. Upper Saddle River, N.J.: Prentice Hall, 1982, Chaps. 4 and 6.

WESTERWERF, K. R., W. P. M. VAN SWAAN, and A. A. C. M. BEENACKERS, *Chemical Reactor Design and Operation*. New York: Wiley, 1984.

A number of example problems dealing with nonisothermal reactors can be found in

SMITH, J. M., *Chemical Engineering Kinetics*, 3rd ed. New York: McGraw-Hill, 1981, Chap. 5.

WALAS, S. M., *Reaction Kinetics for Chemical Engineers*. New York: McGraw-Hill, 1959, Chap. 3.

WALAS, S. M., *Chemical Reaction Engineering Handbook of Solved Problems*. Amsterdam: Gordon and Breach, 1995. See the following solved problems: Problem 4.10.1, page 444; Problem 4.10.08, page 450; Problem 4.10.09, page 451; Problem 4.10.13, page 454; Problem 4.11.02, page 456; Problem 4.11.09, page 462; Problem 4.11.03, page 459; Problem 4.10.11, page 463.

For a thorough discussion on the heat of reaction and equilibrium constant, one might also consult

DENBIGH, K. G., *Principles of Chemical Equilibrium*, 4th ed. Cambridge: Cambridge University Press, 1981.

2. A review of the multiplicity of the steady state is discussed by

LUSS, D., and V. BALAKOTAIAH, in *Chemical Reaction Engineering—Boston*, J. Wei and C. Georgakis, eds., ACS Symposium Series 196. Washington, D.C.: American Chemical Society.

PERLMUTTER, D. D., *Stability of Chemical Reactors*. Upper Saddle River, N.J.: Prentice Hall, 1972.

SCHMITZ, R. A., in *Chemical Reaction Engineering Reviews*, H. M. Hulburt, ed., Advances in Chemistry Series 148. Washington, D.C.: American Chemical Society, 1975, p. 156.

3. Partial differential equations describing axial and radial variations in temperature and concentration in chemical reactors are developed in

WALAS, S. M., *Reaction Kinetics for Chemical Engineers*. New York: McGraw-Hill, 1959, Chap. 8.

4. The heats of formation, $H_f(T)$, Gibbs free energies, $G_f(T_R)$, and the heat capacities of various compounds can be found in

PERRY, R. H., D. W. GREEN, and J. O. MALONEY, eds., *Chemical Engineers' Handbook*, 6th ed. New York: McGraw-Hill, 1984.

REID, R. C., J. M. PRAUSNITZ, and T. K. SHERWOOD, *The Properties of Gases and Liquids*, 3rd ed. New York: McGraw-Hill, 1977.

WEAST R. C., ed., *CRC Handbook of Chemistry and Physics*, 66th ed. Boca Raton, Fla.: CRC Press, 1985.

Unsteady-State Nonisothermal Reactor Design

9

Chemical Engineers are not gentle people, they like high temperatures and high pressures.

Steve LeBlanc

Up to now we have focused on the steady-state operation of nonisothermal reactors. In this section the unsteady-state energy balance will be developed and then applied to CSTRs, plug-flow reactors, and well-mixed batch and semibatch reactors.

We will then discuss reactor start-up, falling off the upper-steady state, the control of chemical reactors, and multiple reactions with heat effects.

9.1 The General Equation

We begin by recalling the unsteady-state form of the energy balance developed in Chapter 8.

$$\dot{Q} - \dot{W}_s + \sum_{i=1}^n F_i H_i|_{\text{in}} - \sum_{i=1}^n F_i H_i|_{\text{out}} = \left(\frac{\partial \hat{E}_{\text{sys}}}{\partial t} \right) \quad (8-9)$$

The total energy of the system is the sum of the products of specific energies, E_i , of the various species in the system volume and the number of moles of that species:

$$\hat{E}_{\text{sys}} = \sum_{i=1}^n N_i E_i \quad (9-1)$$

In evaluating \hat{E}_{sys} , we shall neglect changes in the potential and kinetic energies, and substitute for the internal energy U_i in terms of the enthalpy H_i :

$$\hat{E}_{\text{sys}} = \sum_{i=1}^n N_i E_i = \sum_{i=1}^n N_i U_i = \left[\sum_{i=1}^n N_i (H_i - P V_i) \right]_{\text{sys}} \quad (9-2)$$

Differentiating Equation (9-2) with respect to time and substituting into Equation (8-9) gives

$$\begin{aligned} \text{Transient energy balance} \quad \dot{Q} - \dot{W}_s + \sum_{i=1}^n F_i H_i|_{\text{in}} - \sum_{i=1}^n F_i H_i|_{\text{out}} \\ = \left[\sum_{i=1}^n N_i \frac{\partial H_i}{\partial t} + \sum_{i=1}^n H_i \frac{\partial N_i}{\partial t} - \frac{\partial \left(P \sum_{i=1}^n \frac{V}{N_i V_i} \right)}{\partial t} \right]_{\text{sys}} \end{aligned} \quad (9-3)$$

For brevity we shall write these sums as

$$\Sigma = \sum_{i=1}^n$$

unless otherwise stated.

9.2 Unsteady Operation of CSTRs and Semibatch Reactors

When no spatial variations are present in the system volume, and variations in the total pressure and volume are neglected, the energy balance, Equation (9-3), reduces to

$$\dot{Q} - \dot{W}_s + \Sigma F_{i0} H_{i0} - \Sigma F_i H_i = \Sigma N_i \frac{dH_i}{dt} + \Sigma H_i \frac{dN_i}{dt} \quad (9-4)$$

Recalling Equation (8-19),

$$H_i = H^\circ(T_R) + \int_{T_R}^T C_{pi} dT \quad (8-19)$$

and differentiating with respect to time, we obtain

$$\frac{dH_i}{dt} = C_{pi} \frac{dT}{dt} \quad (9-5)$$

Then substituting Equation (9-5) into (9-4) gives

$$\dot{Q} - \dot{W}_s + \Sigma F_{i0} H_{i0} - \Sigma F_i H_i = \Sigma N_i C_{pi} \frac{dT}{dt} + \Sigma H_i \frac{dN_i}{dt} \quad (9-6)$$

The mole balance on species i is